# STUDIES ON HIGH PERFORMANCE NI-BASED COMPOSITE CATALYSTS FOR PREFERENTIAL METHANATION OF CO IN A SYNGAS

BY

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In

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*Dedicated To My Parents*

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*Dedicated*
*To*
*My Parents*

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In the name of Allah, the Beneficent. The most merciful. Praises and thanks be to Allah, the lord of the worlds, and peace be upon the last messenger, Mohammad, his family and companions, for giving me the help and guidance that enabled me to work successfully.

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# ABSTRACT

FULL NAME: MUHAMMAD BADRUL ISLAM CHOUDHURY.

TITLE OF STUDY: STUDIES ON HIGH PERFORMANCE NI-BASED COMPOSITE CATALYSTS FOR PREFERENTIAL METHANATION OF CO IN A SYNGAS.

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*For the inert activity of methane, methanation catalysts are being used in the process industries to purify gaseous materials. The high performance multi-component methanation catalysts have come to be research objective nowadays for new processes such as Fuel Cell technology and synthesizing clean and high calorific gaseous fuel.*

*This work comprised the preparation of Ni-based multi-component composite catalysts, case studies of reduction properties by using temperature-programmed reduction (TPR) method and performance evaluation testing in a continuous flow micro-reactor. Feed gas mixture to the reactor contains 6% CO, 6% $CO_2$, 44%$H_2$ and 44% $N_2$. The operating conditions are 1 atm pressure and different temperatures within the range of 200°C to 500°C. TPR analysis helped to characterize the effect of precious-metal addition to basic metal oxides and explain the relatively complex spillover mechanism. The four-component methanation catalyst (Ni-$La_2O_3$-Ru-Rh) was found the most active among all methanation catalysts found in literature. In this case of the methanation of CO occurred preferentially at 230°C. Methanation of $CO_2$ occurred after complete conversion of CO. As long as CO presents in the syn gas, methanation of $CO_2$ was retarded.*

*The activity of the catalyst was increased by adding $La_2O_3$ with Ni. $La_2O_3$ with Ni increased Ni dispersion and added basicity. The activity was further increased by addition of trace amount platinum group metals Ru and Rh. These metals enhanced dissociative adsorption of $H_2$, and then reduce the main catalyst component $NiO_x$ by spilltover hydrogen atoms. A good relationship between the results of TPR and catalytic performance for preferential methanation of CO was confirmed.*

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

# ملخص الرسالة

**الإسم: محمد بدر الإسلام شودري**

**عنوان الرسالة: دراسة على الفاعلية العليا لمحفزات النيكل للتفاعل المفضل لأول أكسيد الكربون في غاز التصنيع إلى الميثان.**

**التخصص: الهندسة الكيميائية.**

**تاريخ التخرج: كانون الثاني ٢٠٠٥م**

تم استخدام المحفز الميثيلي في الصناعات لتنقية المواد الغازيه بسبب عدم وجود نشاط للميثان. إن الأداء الفائق للمحفز الميثيلي يعد هدفاً للباحثين في هذه الأيام للعمليات الجديده كتكنولوجيا بطاريات الوقود وتصنيع وقود الغاز النظيف.

يشمل العمل إعداد عينات من حفازات النيكل متعددة العناصر ودراسة خواص الإختزال باستخدام الإختزال الحراري المتزامن (TPR) وتعيين خواص وتقويم الأداء بستخدام مفاعل مصغر متواصل الدفق. خليط الغاز المغذي للمفاعل يتكون من ٦% غاز أول أكسيد الكربون، ٦% غاز ثاني أكسيد الكربون، ٤٤% غاز الهيدروجين و ٤٤% غاز النيتروجين. الظروف التشغيلية هي 1 ضغط جوي ودرجات حرارة مختلفة تتراوح بين ٢٠٠ درجة مئوية و٥٠٠ درجة مئوية. ولقد مكنت طريقة ال TPR من تشخيص تأثير إضافة المعادن النفيسه لاكاسيد المعادن القلوية وشرح ميكانيكية الارتباط. وقد أظهرت النتائج أن الحفاز رباعي العناصر هو الأنشط بين المحفزات الموجودة في المراجع كمحفز. وهنا تتم عملية الميثنة لأول اكسيد الكربون CO بشكل مفضل عند درجة حرارة ٢٣٠ درجة مئوية لثاني اكسيد الكربون $CO_2$ بعد تحويل CO. وبينما كان غاز ال CO موجوداً ضمن غاز التصنيع فإن $CO_2$ الميثنه كان معاقاً.

إن وجود الـ $La_2O_3$ مع الـ Ni يؤدي إلى زيادة الإنتشار السطحي والقاعدية لذالك تزداد فعالية المحفز بإضافة الـ $La_2O_3$ مع الـ Ni. كما أن نشاط المحفز قد ازداد أكثر بإضافة كميات ضئيلة من الروثينيم والرديم من مجموعة البلاتينية. إن هذه المعادن قد زادت من الأدمصاص التفككي لغاز الهيدرجين وبذلك قللت من إستخدام المكون الرئيسي للمحفز $NiO_x$ بواسطة خاصية انسياب الهيدروجين. وقد تم الربط بين النتائج الجيدة للـ TRP والأداء التحفيزي لإنتقاء الميثنة لـ CO.

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# CHAPTER 1

# INTRODUCTION

## *1.1 INTRODUCTION*

The selective catalytic hydrogenation of CO (eq.1) and/or $CO_2$ (eq.2) to form methane is simply called methanation. Methanation chemistry can be described as several independent reactions in which a mixture of carbon oxides and hydrogen are reacted over a methanation catalyst. These reactions are: the methanation reactions, the water-gas shift reaction and the Boudard reaction [1]. For hydrogen to carbon monoxide ratio equal to or greater than 3, the methanation reaction is described as follows:

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O \qquad \Delta H_{298K} = -205\ kJ\ mol \qquad (1)$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \qquad \Delta H_{298\ K} = -113\ kJ\ mol \qquad (2)$$

Reaction (2) can not occur in presence of carbon monoxide [2]. Methanation nowadays has come to be utilized more and more for new process of synthesizing a clean and high calorific gaseous fuel: methane as well as of removing CO to get rid of its detrimental effects. The importance also should be attached to effective use of $CO_2$ for methanation from the viewpoint of a cyclic use of carbon resources whose supply will be more limited in the near future.

Hence a catalyst having a sufficient methanation activity for carbon oxides would be needed.

As we know carbon monoxide and carbon dioxide act as poisons for some process such as ammonia synthesis. Hence, it is necessary to reduce the final amounts of carbon oxides to a very low level. A simple and relatively inexpensive method is conversion of carbon oxides into methane and water. Generally the methane acts as an inert material. Energy consumption is very high for the conventional methanation catalysts, besides their low performance. Taking such viewpoints, novel type Ni-based composite catalyst system (Ni-$La_2O_3$-Ru-Rh) was studied and investigated. Because Ni-based composite (three or four component) catalysts exert very high activity for CO methanation compared to conventional nickel catalysts and, contrary to many other methanation catalysts; the activity of these composite catalysts for $CO_2$ methanation is higher than that of CO methanation [3].

The success or otherwise of catalyst preparation or modification depends on the availability of suitable characterization techniques to determine the condition of catalyst. There are many techniques available for characterization of catalysts including x-ray powder diffraction, electron microscopy, photoelectron spectroscopy, and infrared spectroscopy. However, none of these techniques has proved to be wholly reliable or generally applicable to the characterization of catalyst under working conditions.

Temperature programmed reduction has been widely used in studying the reduction behavior of supported and unsupported catalysts. It is highly sensitive and does not depend on any specific property of the catalyst other than that specifies under study be in reducible condition. The main feature of the method is its capability of

continuously monitoring the consecutive reactions of reducible species at increasing temperatures. It can thus provide information about the dispersion state of the metallic component as well as the metal-support and metal-metal interactions in catalysis, since all of these affect reduction behavior.

Studies and analysis on TPR peak profiles can aid the selection of pre-treatment conditions for oxidic catalyst precursors. The interpretation of TPR curves is usually confined to the discussion of peak maximum temperatures, the number of more or less resolved reduction peaks or the determination of the total hydrogen or carbon monoxide consumption from which the degree of reduction could be determined.

## *1.2 APPLICATION OF TPR*

Understanding reduction behavior is essential for catalyst development. In many cases it is the reduction treatment that creates the active sites of catalyst.

Temperature programmed reduction (TPR) is a convenient and rapid technique that provides qualitative information on the oxidation state of the reducible species and in that sense it is a finger print. The information obtainable from TPR technique are:

- Characterization of redox properties of materials
- Temperature range of consumption of reducing agent
- Total consumption of reducing agent
- Interaction between metal oxide and support
- Indication of alloy formation in bimetallic catalysts
- Mechanism and kinetics of reduction
- The influence of additives on the reduction of a catalytic material.

## *1.3 OBJECTIVE*

The major theme of this thesis is to study the behavior of Ni based multi-component composite catalysts for the preferential removal of CO. In this thesis work the behavior of methanation catalysts, Ni-based composite catalysts supported on θ-alumina, were studied by using Temperature Programmed Reduction (TPR) method and were tested in a continuous flow micro reactor. TPR, giving qualitative and quantitative information from a rapid and a simple experimental procedure, can be successfully used to clarify the cause of increased activity of multi-component supported catalysts; especially metal dispersion and spillover effect. The actual performance of the catalysts was tested in the reactor by continuous flow of a gas mixture containing 6% CO, 6% $CO_2$, 44%$H_2$, and 44% $N_2$ through the catalysts.

The overall objective of studying high performance Ni-based composite catalysts can be set as specific objectives as follows:

1) Studying the performance of Ni based catalysts.
2) Studying the properties of the catalysts for analyzing the high performance
3) Analysis of the Temperature-Programmed Reduction (TPR) profile to elucidate the spillover mechanism of the catalyst
4) Improving the performance of the existing catalysts.
5) Testing the actual performance of catalysts.

# CHAPTER 2

# HISTORICAL DEVELOPMENT

## *2.1 HISTORY OF METHANATION CATALYSTS* [4]

During almost a century, a large number of studies on methanation have been done; however, the trend of these studies shifted in roughly three periods owing to the demand of chemical industries and global environmental anxiety.

**First Stage:** In the first stage, up to the middle of the twentieth century, the reaction had been used to remove trace of CO and $CO_2$ from hydrogen-rich industrial gases, such as those used for ammonia synthesis, because CO sensitively poisons the catalytic activity. In many other catalytic reactions, which aim at the production of targeted compounds, in general, the concentrations of reactants and products are considerably high. The composition of the reactants in these cases is near the reaction stoichiometry, and therefore, the reaction mechanism and kinetic analysis would often obey as Langmuir-Hinshelwood-type ones. On the other hand, in the methanation for CO removal, the composition of the reactants deviates far from the stoichimetry. Furthermore, since the CO concentration decreases to an extremely low level with an increase of the reaction degree, the catalytic activity must be very high to eliminate CO

completely. Although methanation seemed to be very simple, it had various basic problems. Indeed, these kinds of reactions under deviated conditions have become more important, especially in the last quarter of the twentieth century. A wide variety of subjects such as $NO_x$ and $SO_x$ eluted from automobiles and stationary generating sources, removal of offensive odors, and ultrahigh purification of gases for use of in electronics production are covered in this category.

In the first half of 1950s, equipment used for gas chromatography was commercialized, and it has contributed to the precise analysis of gaseous and volatile materials. Methanation was used for an intriguing application for analysis by gas chromatography. Trace of carbon oxides can be analyzed more precisely after methanation by a FID-type detector used in gas chromatography than by a TCD-type detector.

Reactants and products of methanation are simple, and even under atmospheric pressure, it occurs at a medium temperature range of around 470-730 K, and therefore, many academic studies on this catalytic reaction had been done. Summarizing the accumulated knowledge during the period from the first publication to 1954, Greyson[5] gave the devoted and excellent review on fundamental subjects based on a total of 63 references. These were thermodynamic data of this reaction system, effect of kind of catalyst metals and supports, effect of reaction conditions, poisoning by sulfur, and effect of catalyst preparation methods. Furthermore, the potential of methanation for being applied to the synthesis of a high caloric gaseous fuel from syngas was also mentioned.

**Second Stage:** Decades after the end of the Second World War, economy and industrialization of the world developed extensively, and energy consumption

increased exponentially. Furthermore, city gas ─so far coke oven gas was used ─had been replaced by high caloric and clean natural gas in advanced countries, and consequently, the importance of methanation as the process for the production of substituted natural gas(SNG) from syngas, which can be produced from abundant resources such as coal and water. Various types of industrial processes for the production of SNG were designed, and some of them were practically commercialized [6]. Different from the first stage, in the second stage, methanation was positively taking into account the application to the production process of methane. Including the methods and devices to control the large exothermic heat of the methanation reaction, dependence of the reaction conditions such as flow rate of the feed, and detailed composition of the products on different kinds of catalysts, in 1973 Mills and Steffgen [1] reviewed modern methanation based on 130 references. Reflecting this trend, in 1980, Trimm [7] summarized the requisites for the industrial methanation catalyst based on 38 references published mainly in 1970s. On the other hand, G. Henric-Olivé and S. Olivé [8] reviewed methanation from the view point of reaction mechanism based on the results of the studies on FT synthesis and $C_1$ chemistry. Carbide mechanism, CO insertion mechanism, and inverse H/D isotope effects are involved as the typical proposed reaction mechanisms and related reaction characteristics.

Investigation of energy-saving devices and processes was also carried out in this period. A typical one known as EVA-ADAM process [9] was achieved in Germany by applying methanation. The process consists of two reaction systems. The first one(EVA) is endothermic steam reforming of methane, i.e., inverse reactions of equations 2.1 and 2.2.

$$CO + 3\,H_2 = CH_4 + H_2O \qquad \Delta H_{298\,K} = -205\ kJ/mol \qquad (2.1)$$

$$CO_2 + 4\,H_2 = CH_4 + 2\,H_2O \qquad \Delta H_{298\,K} = -113\ kJ/mol \qquad (2.2)$$

This requires a large amount of energy at a temperature level of about 1220 K, which is supplied from the high temperature gas furnaces. The second one (ADAM) is exothermic methanation of CO and $CO_2$, i.e., reactions of equations 2.1 and 2.2, where heat is set free over a wide range of temperature. The energy taken up in EVA is transformed into a cold $H_2$-rich gas that is transported to ADAM where heat is realeased according to the requirements of the heat market. This kind of energy transportation system is called chemical heat pipe.

**Third stage:** The Roman's club's report *Limit of Growth* presented in 1972 had already warned against the global warming caused by the accumulation of huge amount of $CO_2$, which is emitted from the combustion of fossil fuels. The 1973 Petroleum Crisis brought about an awareness of the necessity of energy saving of developing in alternative energy sources other than petroleum. Reflecting these trends, at the beginning of this period, conventional FT synthesis was reconsidered and study of $C_1$ chemistry progressed extensively. In this context, methanation of CO and $CO_2$ mitigation, is that the reaction needs a huge amount of expensive hydrogen. One of the rational approaches to solve this problem is that methane or natural gas be used as reducing reagent for $CO_2$ instead of $H_2$; in other words, this reaction is $CO_2$- reforming of methane, expressed as equation 2.3.

$$CO_2 + CH_4 = 2\,H_2 + 2\,CO \qquad \Delta H_{298\,K} = +247\ kJ/mol \qquad (2.3)$$

Studies on methanation of $CO_2$ have been reviewed recently by Halman and Steinberg [10]. The reaction expressed by equation 2.3 has been reviewed most recently by Inui [11]. However, since description on the significance and concrete characteristics of

those catalysts and related reactions seems to be still in sufficient, the focus of this term is concentrated on the recent advances in rapid $CO_2$ methanation, CO-$CO_2$ co-methanation.

### 2.1.1 Significance of Methanation Reaction as the Production of Energy Transportation Media

Since in $CO_2$ methanation, $H_2$ needed is four times of $CO_2$, it seems to be disadvantageous from the viewpoint of energy and economical considerations. However, as far as it is known the formation rate of methane by catalytic hydrogenation of $CO_2$ can be realized far beyond all other methods for chemical conversion of $CO_2$. The large consumption of hydrogen per unit $CO_2$ mole corresponds to the fact that the accumulation of internal energy into methane molecules is large and the methane synthesized by hydrogenation of $CO_2$ is expected to act as the transportation media of the energy injected into the reaction. When the rapid $CO_2$ methanation progress at a low temperature range of around 470-730 K, the large exothermic reaction heat itself can be used and, furthermore, when the methane formed is used as fuel, a high temperature, even 1300 K, can be obtained. Therefore, it is thought that the rapid $CO_2$ methanation is significant as one kind of the chemical heat pump by which a low temperature, i.e., value energy, can be transformed into a high temperature, i.e., high value energy, through chemical reactions.

### 2.1.2 Development of High Performance Catalyst for $CO_2$ Methanation

It has been known that the rate of $CO_2$ hydrogenation on a nickel catalyst, even with the co-existence of promoters is less than that of CO. This had been confirmed by comparative studies on the kinetics of CO and $CO_2$ methanation over a commercial supported nickel catalyst [12], and powdery Co, Ni, and inter-metallic compounds such as $CeNi_2$ and $CeAl_2$ [13]. Supported Ru catalyst, which is known as the most active catalyst for the Sabatier reaction [14], was tested for $CO_2$ methanation under a medium reaction pressure [15] and was used for the kinetic study of $CO_2$ methanation at atmospheric pressure. However, considerable minor activities were observed in these studies [16].

Inui and co-workers have studied $CO_2$ methanation since 1970s, and developed the Ni-based three-component composite catalyst supported on spherical silica having bimodal meso-macro pore structure [17]. The catalyst contained $La_2O_3$ by 1/5 mol of Ni, and Ru by 1/30 mol of Ni. The Ni-$La_2O_3$-Ru catalyst exhibited the high conversion rate to synthesize methane exclusively. As compared in Figure 2.1, the methanation activity of the three-component catalyst is very high, far beyond the summation of the activity of each catalyst component.

Adsorption capacity of the Ni-based catalyst for carbon oxides, especially $CO_2$, is increased markedly by addition of $La_2O_3$, whereas $H_2$ uptake remained unchanged. On the other hand, by the addition of Ru to the two-component catalyst, $H_2$ uptake increased two times [3].

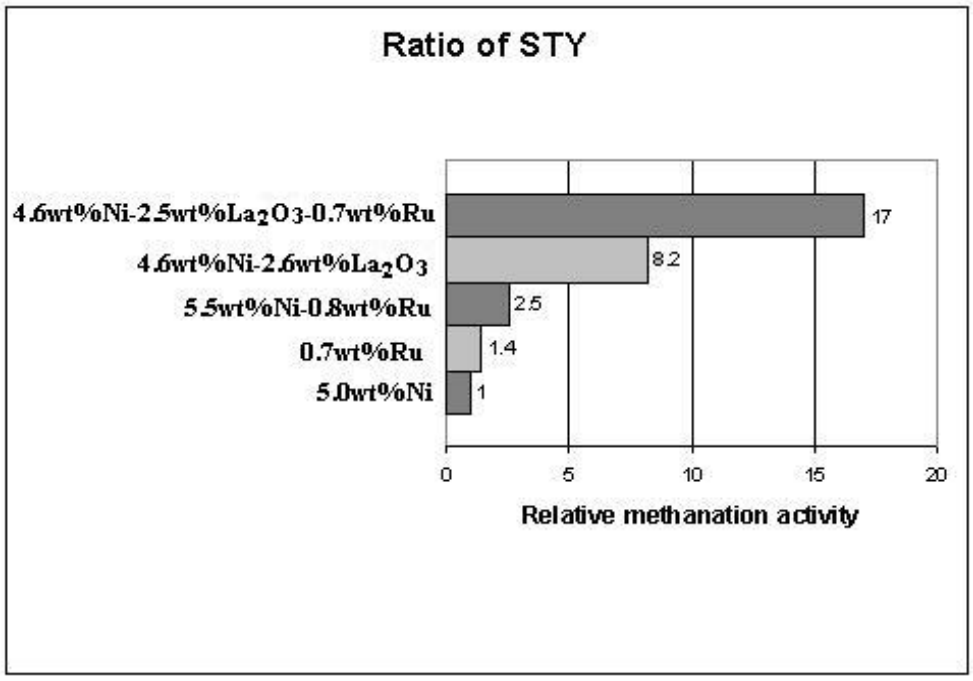


**Figure 2.1: Activity of $CO_2$ methanation for the Ni-$La_2O_3$-Ru catalyst and catalysts of various combinations of the components.**

**Activity is expressed by the ratio of space-time yield (STY) of methane. The activity ratio 1 corresponds to methane STY 0.56mol/(L.h). Reaction conditions: 6mol% $CO_2$, 18 mol% $H_2$; space velocity (SV) 10,000$h^{-1}$; pressure 0.1MPa; temperature 500K. [17].**

The change in adsorption characteristics of three kinds of catalysts for each reactant was measured and is summarized in table 2.1.

Table 2.1: Relative Adsorption amounts of Reactants in Methanation [a]

| Catalyst | Relative adsorption amount at 298K | | |
|---|---|---|---|
| | $H_2$ | $CO_2$ | CO |
| 5.0wt% Ni | 1.00[a)] | 1.00[b)] | 1.00[c)] |
| 4.6wt%Ni-2.6wt% $La_2O_3$ | 1.08 | 3.18 | 1.77 |
| 4.3wt%Ni-2.5wt%$La_2O_3$-0.7wt%Ru | 2.02 | 2.63 | 1.91 |

[a)]Adsorption amount (ml/ml cat.): a) 0.291, b) 0.209. c) 0.445

The effect of the combination of these components was observed more distinctly by the observation in dynamic state during the reaction [17]. As shown in Figure 2.2, the partial pressure dependence on $CO_2$ methanation for the three-component catalyst, kept nearly the same order in $CO_2$ but rather increased in $H_2$, although the space-time yield (STY) increased ≈ 30 times compared than to those on Ni single-component catalyst. This indicates that especially the adsorption rate of $H_2$ was enhanced remarkably during the reaction by the addition of Ru.

The activity of a three-component catalyst is far beyond the sum of the constituent single-component catalysts. Its activity is higher than that of a highly concentrated (3.3%) Ru catalyst. However, when $La_2O_3$ which by itself do not have enough activity for methanation, was added to Ni, the activity increased markedly. Moreover, the incorporation of Ru into Ni + $La_2O_3$ greatly enhanced the activity. Again methanation decreases with the decrease of diffusivity.

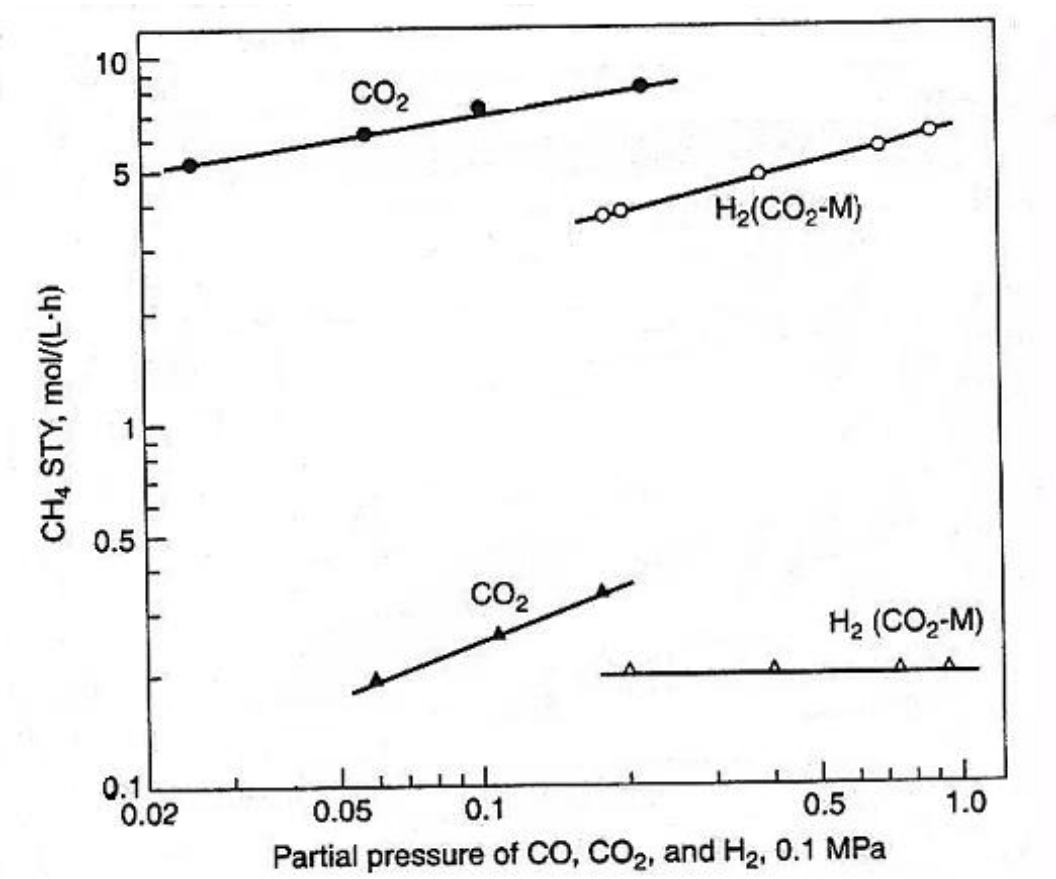


**Figure 2.2: Partial pressure dependence in $CO_2$ methanation on the Ni catalyst and the Ni-$La_2O_3$-Ru catalyst.**

**(Triangle) Ni catalyst; (Circle) Ni-$La_2O_3$-Ru catalyst; Reaction conditions: SV 10,000$h^{-1}$; temperature 475K; pressure 01 MPa; diluent of the reaction gas was $N_2$.[17]**

The activity is low for large diffusivity with small surface area. Again with large surface area with small diffusivity the activity is extremely slow. Maximum activity was obtained by macro-meso bimodal pore catalyst whose surface and effective diffusivity both was large.

The authors (Inui et al.) conclude that the activity of the composite catalysts with the rate of $CO_2$ methanation is as follows. For substrates of iron-group metals, the order is: Ni>Co>Fe; for the combined rare earth oxides: $La_2O_3$>$Ce_2O_3$; and for the combined platinum-group metals: Ru>Rh. Maximum activity was obtained with the Ni+$La_2O_3$+Ru combination.

The cause of the high performance was elucidated as follows: the adsorption capacity of the catalyst for $CO_2$ was increased by the weak basisity of $La_2O_3$ and hydrogen adsorption was remarkably enhanced by combining Ru, which worked as the porthole of hydrogen spillover [17].

### 2.1.3 Simultaneous Methanation of CO and $CO_2$

Carbon dioxide is formed as a by-product in the production process of synthetic gas by the steam reforming reaction of petroleum naptha or liquedified petroleum gas, but it is wasted as a nonreactive material. With regard to this process, a case even appeared in which $CO_2$ and $H_2O$ during CO methanation. However, importance should be attached to the effective use of $CO_2$ for methanation from the view point of cyclic use of carbon resources.

In a study Tomoyuki Inui, Masaki Funabiki and Yohinobu Takegami studied adsorption of Ni-based Methanation Catalysts using the continuous flow method [3].

They prepared five kinds of catalysts. These were single-,by- and tri-component catalysts of the Ni-based composite catalyst system, Ni + $La_2O_3$ + Ru, supported on a spherical silica having meso and macro bimodal pore structures.

They suggests that at 25°C hydrogen is adsorbed by the metal but not by the carbon; on heating from 25°C to 350-400°C in $H_2/N_2$ hydrogen is adsorbed by not only the metal but also the carbon; on heating in $N_2$ at 350-400°C hydrogen is desorbed rapidly from the metal but only slowly from carbon.

The authors conclude that combining $La_2O_3$ with Ni increased the adsorptions of both hydrogen and carbon oxides, especially carbon dioxide; where as adding Ru with Ni or Ni + $La_2O_3$ markedly increased the $H_2$ adsorption at a given hydrogen partial pressure. The former was interpreted as an increase of the Ni dispersion by $La_2O_3$ and its basicity and the latter supports the hydrogen spillover mechanism.

In another study the methanation be the use of mixed gas containing 6% CO, 6%$CO_2$ and 88% $H_2$ was carried out by Inui et all, respectively, on the three kinds of catalysts with a space velocity of 11,400/h [2]. The reaction temperature was raised until carbon oxides were completely converted.

The temperature dependence of CO and $CO_2$ conversion for each catalyst is shown in Figure 2.3. The rate of solo methanation of $CO_2$ is greater than that of CO on the Ni-$La_2O_3$ or Ni-$La_2O_3$-Ru catalyst in the lower reaction temperature range. Nevertheless, in coexistence of CO and $CO_2$ methanation of CO occurred preferentially on every catalyst, and $CO_2$ methanation first preceded after CO was almost completely consumed.

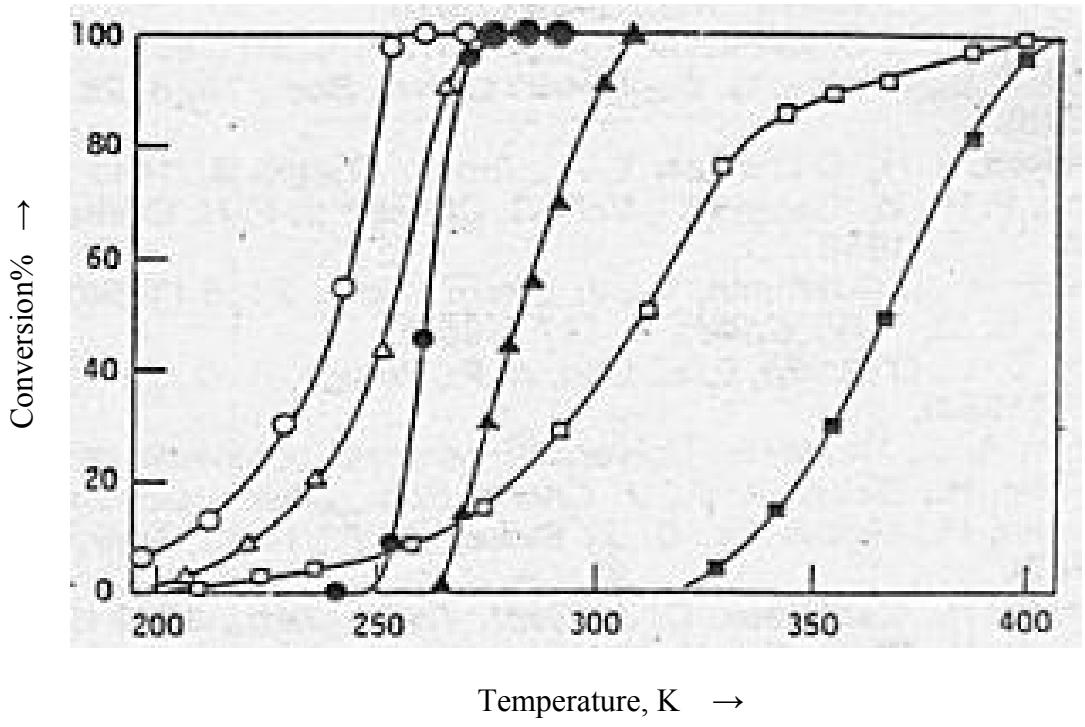


**Figure 2.3: Temperature dependence of CO and $CO_2$ conversion in the co-methanation on various catalysts.**

**(Circle) Ni-$La_2O_3$-Ru; (triangle) Ni-$La_2O_3$; (square) Ni; (Open symbol) CO conversion;**

**(filled symbol) $CO_2$ conversion. [2].**

Especially, on the bi- and tri- component catalysts, $CO_2$ methanation followed at an accelerated rate, and a complete conversion of both CO and $CO_2$ was achieved at such low temperatures as 543 K (Ni-$La_2O_3$-Ru) and 573 K (Ni-$La_2O_3$). These indicate that the adsorption strength of CO during the reaction is far stronger than that of $CO_2$ on every catalyst, and the existence of CO inhibits $CO_2$ methanation.

The authors concluded that, in the co-methanation of CO and $CO_2$ using Ni-$La_2O_3$-Ru catalyst, the $CO_2$ methanation is retarded unless CO exists, in spite of the fact that in solo-methanation, $CO_2$ has a higher activity than CO. However, with a decrease of CO concentration by an increase in the reaction rate at high temperatures, the surface-carbon species decreases and retardation of the CO-methanation itself is released. Then the catalyst temperature rises and the temperature differences between the catalyst and the gas phase increases. This state causes $CO_2$ methanation to reach a complete conversion in addition to the complete conversion of CO.

### 2.1.4 Hydrogenation activity

In 1978 Tomoyuki Inui, Kiyokazu Ueno, Masaki Funbiki, Masatoshi Suehiro, Tadashi Sezume and Yoshinobu Takegami studied synergic effect of composite catalysts on the direct hydrogenation of carbon [18]. Their objective was to find the effective catalyst system and reaction mechanism in agreement with the gas-solid catalytic reaction. The three-component catalyst, Ni or Co as the catalyst substrate combine with a small amount of $La_2O_3$ and a platinum group meta such as Ru, exerted a synergic effect on the hydrogen of the active carbon at temperatures within the range 300-800°C.

A comparison of hydrogenation activity for various single component catalysts was shown in Figure 2.4. After the decomposition and reduction of the catalyst-metal salt, methane formed exclusively at temperatures above 300-400°C. The hydrogenation rate initially increased with elevated temperature and then decreased after its maximum value as shown in Figure 2.4. The order of hydrogenation rate shown was: Ni> Co> Ru> Rh> Pt.

Temperature dependence of the hydrogenation rate on each catalyst of this system is presented in Figure 2.5, where $La(NO_3)_3.6H_2O$ was used as the source of $La_2O_3$. Contents of La and Ru in the three-component system were set at atomic ratio of 0.2 and 0.5 respectively, of the substrates Ni. The ammonia-vapor treatment was conducted before the heat decomposed of salt in all case.

As shown in Figure 2.5, $La_2O_3$ itself had very low activity; however, when combined with Ni, the overall was considerably enhanced. Moreover, when a small amount of Ru, whose activity was rather small compared with the nickel in the system, was combined with Ni+$La_2O_3$, an additional enhancement of the activity was observed. Further, the higher the activity of the catalyst, the more it increases the reaction at low temperatures and attains the maximum rate at low temperatures, and also produces a larger total amount of methane formation or a conversion of active carbon below 800°C.

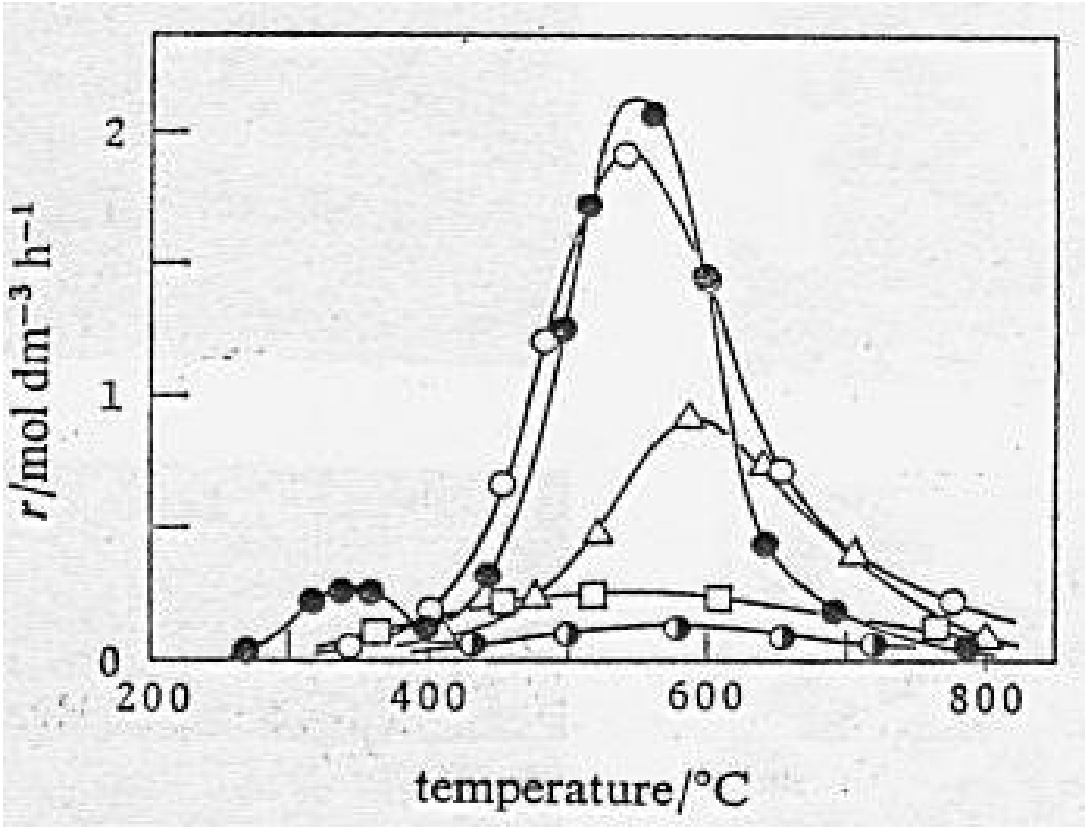


**Figure 2.4: Comparison of hydrogen activity for various single-component catalysts: •, Ni; o, Co; Δ, Ru; □, Rh; ◑, Pt.[18]**

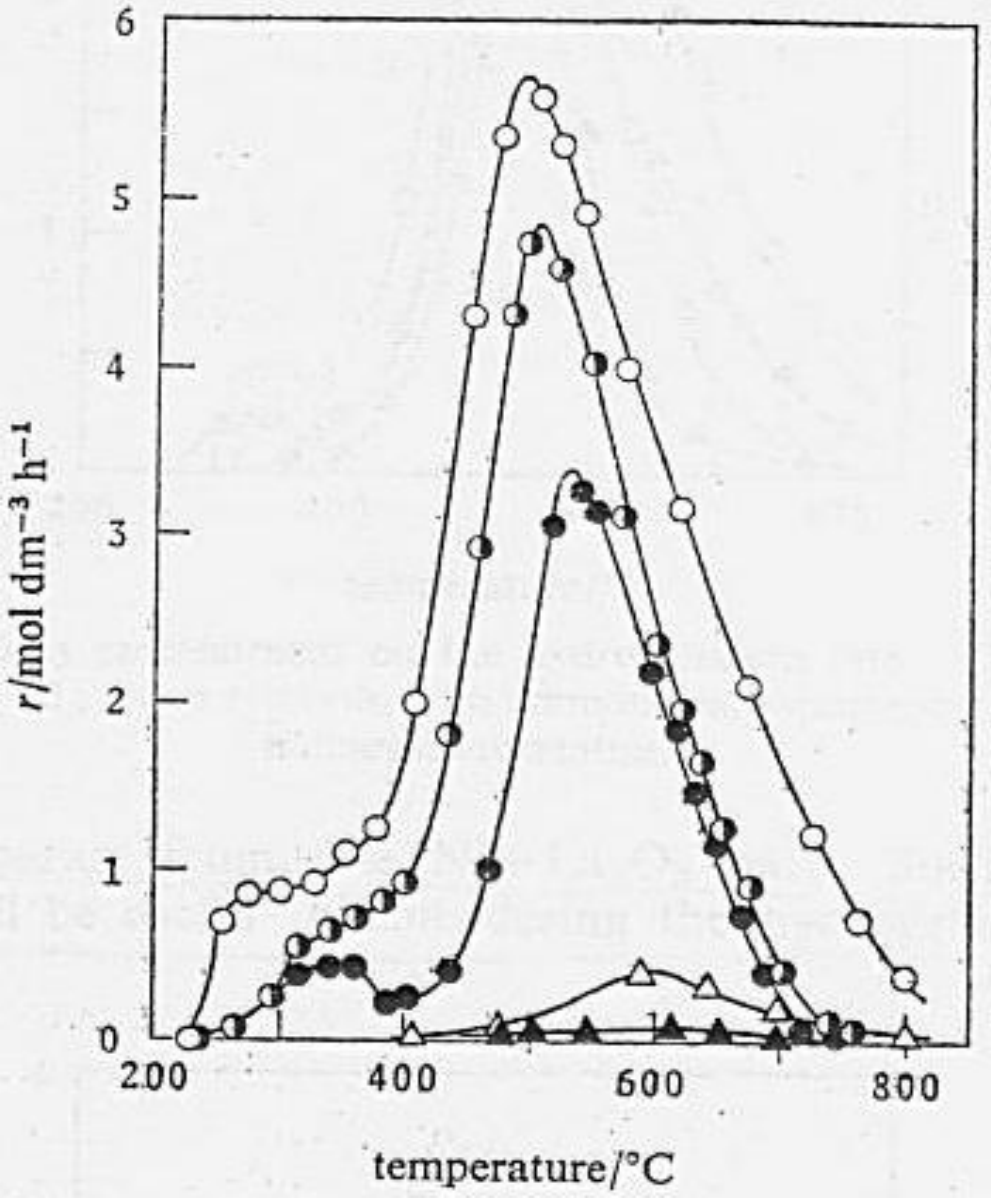


**Figure 2.5: Comparison of hydrogen activity among various catalysts of the Ni+$La_2O_3$+Ru system.**

**○, 4.6% Ni+2.5% $La_2O_3$+1.2% Ru; ◑, 4.6% Ni+2.5% $La_2O_3$; ●, 5% Ni; △, 1.2% Ru;**

**▲, 2.8% $La_2O_3$. Heating rate, $10^0$C $min^{-1}$; hydrogen concentration, 10% [18].**

The effect of ammoniacal treatment is shown in Figure 2.6. In the case of both Ni and Co+$La_2O_3$ that were treated the maximum rate increased by 1.6 times compared with the untreated catalyst.

With the ammoniacal treatment, ammonium nitrate is partially formed and its decomposition at ≈ 200°C helps to accelerate the metal-nitrate decomposition at lower temperature. Thus a higher metal dispersion, bringing about a higher activity, might be achieved.

The order of the preparation procedure was particularly important in the three-component system. When $RuCl_3$ was impregnated onto active carbon simultaneously with $Ni(NO_3)_2$ and $La(NO_3)_3$, the over all activity seemed to lower the activity of Ni+$La_2O_3$, as shown in Figure 2.7. When $RuCl_3$ was doped on to the Ni+$La_2O_3$ – supported active carbon, the resulting activity was also decreased. When only metallic Ru had been previously dispersed on the active carbon a synergic effect was observed.

In conclusion they said that, the co-existence of $La_2O_3$ increases the degree of dispersion of the Ni and the adsorption capacity for hydrogen. Ni + $La_2O_3$ acts as a hydrogen acceptor and the dispersed particles of Ru, which have a fast adsorption rate for hydrogen, play the role of transport agent for hydrogen spillover. Furthermore, the part of the catalyst in close contact with carbon acts as transport agent for the hydrogen spillover to carbon, which itself has a minor hydrogen-adsorption capacity at the reaction temperature, achieving a smooth intake of hydrogen from the ambient gas phase into the carbon-solid phase.

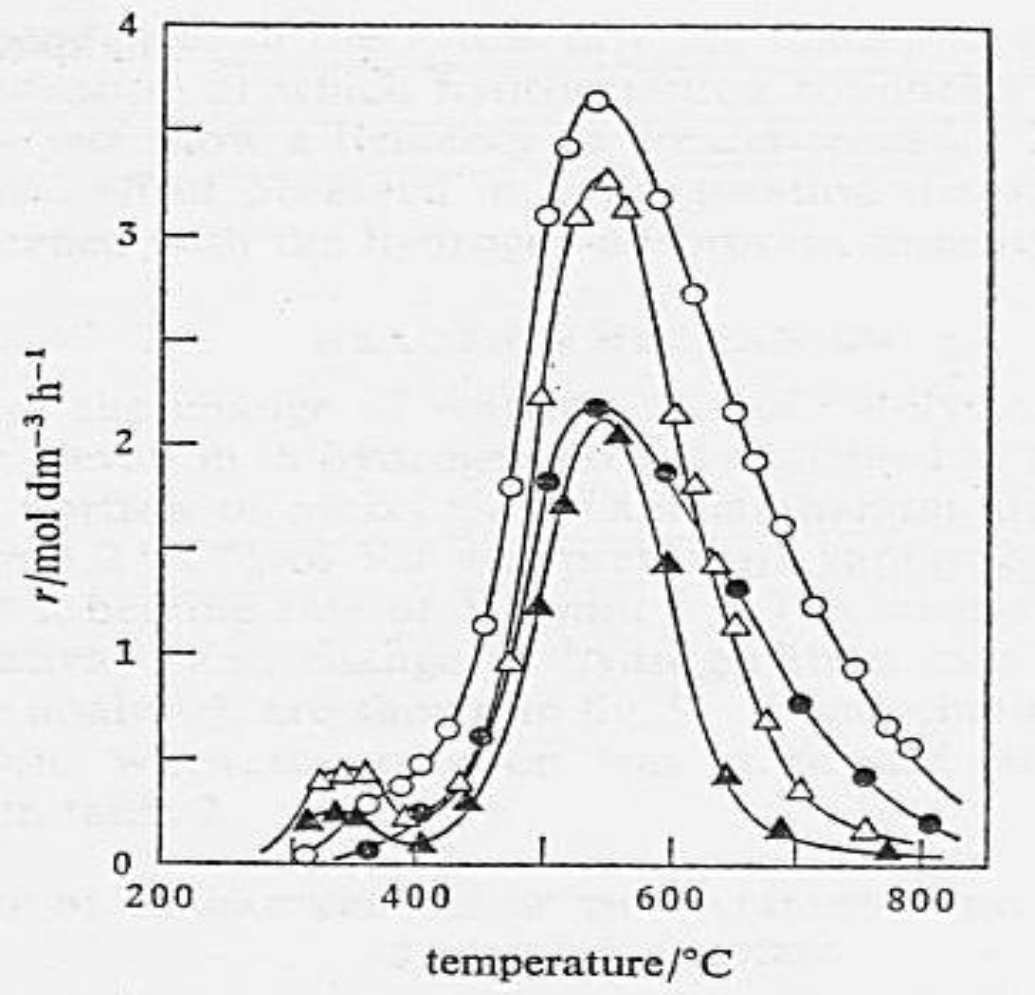


**Figure 2.6: Effect of ammonia pretreatment on the hydrogenation rate. Circles, 5.0 Co+2.7% $La_2O_3$; triangles, 5.0% Ni; open symbols, with ammoniacal treatment; closed symbol, without ammoniacal treatment [18].**

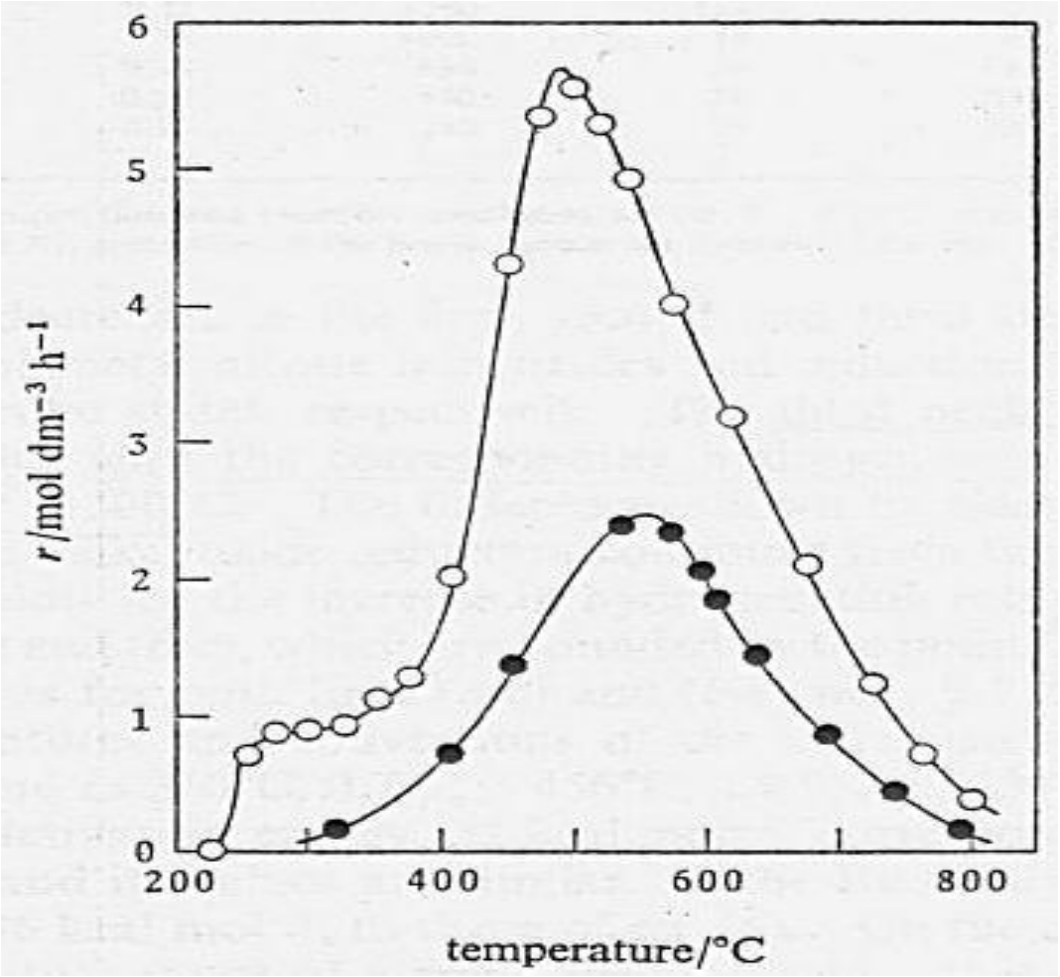


**Figure 2.7: Effect of preparation procedure on the hydrogen rate in the case of the three-component catalyst.**

**Catalyst, 4.6% Ni + 2.5% $La_2O_3$ + 1.2% Ru; ●, mixed solution of the three components was impregnated; ○, nitrates of nickel and lanthanum were impregnated additionally onto the Ru-supported active carbon particles [18].**

Inui et al. investigated the influence of the pore structure of Alumina support on the dispersed Nickel particle size and $CO_2$-methanation activity [19]. They observed changes with calcinations temperature in support properties such as BET surface area and effective diffusivity. Using these calcined aluminas as supports, Ni-$La_2O_3$ catalysts were prepared by impregnation method and the correlation between the pore structure of the support and the activity of $CO_2$ was examined. They found that with the increase of calcinations temperature, BET surface area decreases and diffusivity increases.

They also found that at higher temperatures the crystallite size became larger. The increase in the pore diameter must be the main reason for the increase in crystallite size because of the marked increase in the impregnated solution volume of the pore. For some alumina supports when calcined at 700°C and 910°C, the metal-particle size was as large as or, sometimes, larger than the average pore diameter. Therefore, mesopores, in other words, the pass ways of the reaction gases, would be obstructed by the deposited metal particles, and the diffusivity of the catalyst must be smaller than that of the support. On the contrary, when the supports were calcined at 1060°C and 1130°C, the metal-particle size was much smaller than the average pore diameter, and the reaction gases could pass through readily. The particle size of the supported metal (here Ni) depends not only on BET surface area but also diffusivity that would affect the drying stage of the impregnation solution. Thus there should be an optimum calcinations temperature to get proper balance between diffusivity and metal particle size.

The authors concluded that the catalyst using a support calcined at 1060°C exhibited the highest activity for methanation. At about this temperature, Ni-particle size was small and at the same time diffusivity was high.

## 2.2 HISTORY OF SPILLOVER

Spillover in catalysis was initially considered as a phenomenon occurring on a metal supported on an oxide and concerning mainly the hydrogen reactant. The phenomenon of spillover was defined at the 2nd International Symposium on Spillover as follows; “Spillover involves the transport of an active species which are adsorbed or formed on a first phase onto another phase that does not adsorbed or form the species under the same condition.”

Hydrogen can be absorbed with dissociation on a metal supported on an oxide and surface-diffuse, “spillover”, to react at some distance from the metal [20]. However the definition of spillover should be now extended to include the mobility of sorbed species from one phase on which it is easily adsorbed onto another phase where it does not directly adsorbed [21].

It is now well known, since the reviews on Spillover [21], that a seemingly inert oxide support, such as silica or alumina, can acquire catalytic activity for hydrogen and other transformations of hydrocarbons after activation by spillover of hydrogen (usually 430°C) followed by the separation of the activating metal (Pt or Ni). The spilled over hydrogen does not indeed create catalytic centers on the surfaces of initially non catalytic oxides which can then use molecular hydrogen as the reactant.

An example of the modification of catalytic properties of silica by hydrogen spillover (from $Pt/Al_2O_3$ which is afterwards separated) is well evident in the reaction of cumene in an inert atmosphere at 400°C [22]. Non-activated by spillover silica is able to crack cumene in an inert atmosphere at 400°C into propene and benzene which in turn are cracked into$<C_3$ hydrocarbons and elements ($C+H_2$). But this secondary

cracking which is detrimental to the formation of valuable products is not intense on this non-activated by spillover support. In particular, benzene is not much involved in this secondary cracking. Now, for the spillover activated silica, propene is more stable than benzene and the secondary cracking (with coking) consumes benzene much more than propene. For the reaction carried out at 170°C on the activated silica both propene and benzene are severely cracked into C+ $H_2$ whereas non-activated silica is inactive at this temperature. Therefore, the change of the selectivity from cracking (for non-activated silica) to coking(for activated silica) must be borne in mind for any metal catalyst supported to an oxide because the support may become activated by hydrogen spillover and change the product selectivity from valuable cracking hydrogenated products to cocking products($CH_4$)[23].

It is of interest to underline that in the previous example the spilled over hydrogen was able to create active sites onto the acceptor oxide phase, prior to the reaction. The metal activator was then separated from the acceptor and the spilled over hydrogen was no longer furnished during the reaction.

### 2.2.1 Hydrogen Spillover

Spilt over hydrogen species are unanimously believed to be mono atomic, electrically charged or neutral migrating particles, such as protons $H^+$, hydrides $H^-$, radicals $H^\cdot$, and radical like bound species H─.

**Non charged H species:** The vast majority of the literature published on the nature of the spilt over H species, concludes in favor of the migration of a mono atomic neutral particle as a free radical **H**$^\cdot$ or as a bound atom like **H-** .Proton NMR

experiments performed on Pt supported catalysts evidenced a atomic migration as described first by Sheng and Gay [24] and later by Lenz et al. [25].

**Charged H species:** Most of the published results advocate the proton migration in an adsorbed state as described by Levy and Boudart [26] who studied the influence of co-catalysts exhibiting different proton affinities. Electrical conduction measurements led Khoobiar et al.[27] on $Rh/TiO_2$ conclusion that on alumina, the spilling hydrogen was protonic. Homolytic as well as heterolytic splitting of $H_2$ can be envisaged to give birth to the spilled over entity. However even when charged species are involved, they are believed to come from a hemolytic breakage of the bond in the meaning already developed by Khoobiar where the following scheme summarizes the whole phenomenon.

$$H_2 \rightarrow 2H^{\cdot} \rightarrow 2\ H^{+} + 2e$$

### 2.2.2 Spillover Effect for rapid catalytic reactions [28]

In a study Inui showed precious metals adhered on the surface of Cu as an island state enhanced the rates of both the reduction of pre-oxidized surface and propylene oxidation. This indicates that small amounts of a metal which is more difficult to oxidize than Cu having a dispersed structure on a surface of Cu surface substrate exhibit a spillover of the reactant gas and perform the role of initiation nuclei for reaction with the surface oxygen.

In the same study the author showed that rapid methanation of carbon dioxide occurs due to the spillover effect of by adding trace amount of platinum group precious metals onto conventional methanation catalyst. He showed that on three component

catalyst (Ni-$La_2O_3$-Ru), the rate of methanation of $CO_2$ is about seventeen times greater than that of conventional Ni catalyst. Even by adding trace amount of Ru on Ni, the rate of methanation increased by 2.5 times.

In the same journal the author showed that due to the spillover effect, this three component catalyst (Ni-$La_2O_3$-Ru) causes the rapid catalytic reaction for complete elimination of oxygen in hydrogen gas and rapid reforming of methane to hydrogen and carbon monoxide.

### 2.2.3 Spillover Methanation Mechanism

The studies of methanation support the mechanism involving a back spillover of the methoxy species towards metal part of the catalyst, where it is transformed into methane. A scheme of the mechanism is given in Figure 2.8 and derived from the paper of Palazov et al. [29] for a Pd/$Al_2O_3$ catalyst.

Figure 2.9 shows the dissociated hydrogen atom spilt over to the surface of a four-component catalyst [30]. Little amount of platinum group metals, Rh and Ru, are increased the activity of spillover of hydrogen.

From the literature studied it is seen that the multi-component composite catalysts have higher activity than single or bi component catalysts due to the spillover effect. Therefore, much emphasis should be given on multi-component catalysts for further modification or improvement of the performance and selectivity. Modern temperature programmed method for characterizing the catalyst can help greatly for further development. Unfortunately very few works, almost none, were done on characterizing three or more-component composite catalysts by TPR method.

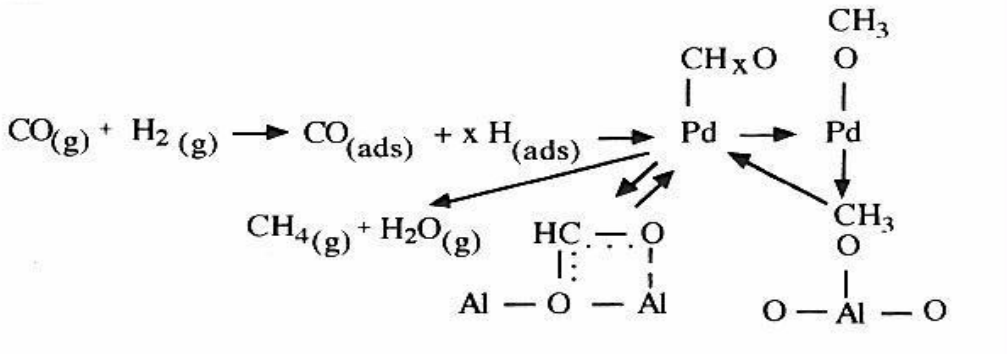


**Figure 2.8: Methanation of CO via a CHxO spillover species on $Pd/Al_2O_3$ catalyst at T≈135°C [29]**

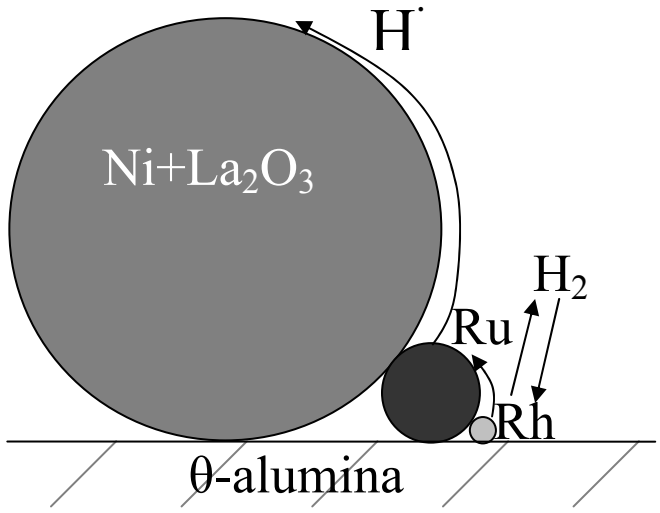


**Figure 2.9: Hydrogen Spillover on four-component methanation catalyst [30]**

## *2.3 THEORY OF TEMPERATURE-PROGRAMMED REDUCTION (TPR)*

### 2.3.1 Thermodynamics of reduction

Reduction is an unavoidable step in the preparation of metallic catalysts. It is often also a critical step, because if it is not done correctly the catalyst may sinter or may not reach its optimum state of reduction. The reduction of a metal oxide $MO_x$ by $H_2$ is described by the equation:

$$MO_x + H_2 \longrightarrow MO_{x-1} + H_2O \qquad (1)$$

Thermodynamics predict under which conditions a catalyst can be reduced. As with every reaction, the reduction will proceed when the change in Gibbs free energy, $\Delta G$, has a negative value. Equation (2) shows how $\Delta G$ depends on pressures and temperature:

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{H_2O}}{P_{H_2}}\right) \qquad (2)$$

where

$\Delta G$ is the change in Gibbs free energy for the reduction

$\Delta G^\circ$ is the same under standard conditions

*n* is the stoichiometric coefficient of reaction

*R* is the gas constant

*T* is the temperature

*p* is the partial pressure

If one reduces the catalyst under flowing hydrogen, the reaction product water is removed effectively and the second term in equation (2) is therefore always negative. For many oxides, such as those of cobalt, nickel and the noble metals, $\Delta G°$ is already negative and reduction is thermodynamically feasible. All one has to do is find a temperature where the kinetics is rapid enough to achieve complete reduction. Figure 2.10 gives an impression on the applicability for several oxides.

Although $\Delta G°$ is positive for a number of oxides such as $V_2O_5$, ZnO and $Fe_2O_3$, the reduction is of these oxides is still thermodynamically feasible because the ratio of partial pressures in equation(2) becomes sufficiently small at elevated temperatures and a high total flow rate since the water formed is constantly swept out of the system. Therefore, most of the interesting catalytically active oxidic phases can be analyzed, while the non-reducible ones are mainly the support oxides.

### 2.3.2 Reduction Mechanism

#### i) Bulk Oxides

Here the process, by which a sphere of metal oxide is reduced, directly to the metal, in stream of flowing hydrogen is described. It is common to observe the degree of reduction as function of time for various temperatures and pressures of hydrogen.

Reduction reactions of metal oxides by hydrogen start with the dissociative adsorption of $H_2$, which is a much more difficult process on oxides than on metals. Atomic hydrogen takes care of the actual reduction.

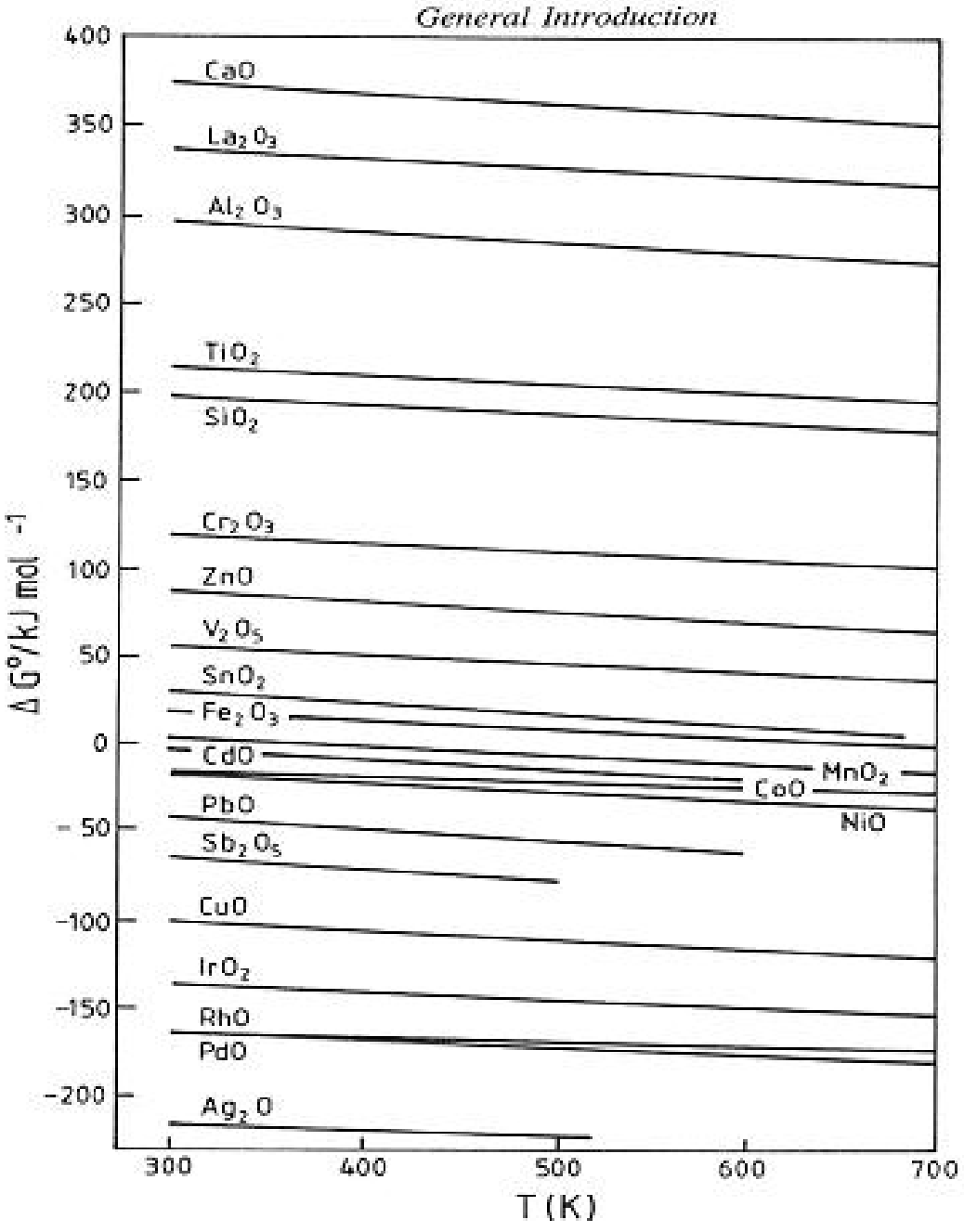


**Figure 2.10: Standard free energy ΔG° as a function of temperature for the process: $MO_x + H_2 \longrightarrow MO_{x-1} + H_2$ [31].**

Depending on how fast or how slow the dissociative adsorption is in comparison to the subsequent reduction reactions that comprise diffusion of atomic hydrogen into the lattice, reaction with oxygen and removal of the hydroxyl species formed, two limiting cases are distinguished.

**The contracting sphere model**

If the initiation step, the activation of $H_2$, is fast, as many be the case on the noble metal oxides or highly defective oxide surfaces, the shrinking core or contracting sphere model applies (Figure 2.11). The essence of this model is that nuclei of reduced metal atoms form rapidly over the entire surface of the particle and grow into shell of reduced metal. Further reduction is limited by the transport of lattice oxygen out of the particle. The extent of reduction increases rapidly initially, but slows down as the metal shell grows.

**Nucleation**

The nucleation model represents the other extreme. Here dissociation of hydrogen is the slow step. Once a nucleus of reduced metal exists, it acts as a catalyst for further reduction, as it provides a site where $H_2$ is dissociated. When the oxide and hydrogen come into contact the reaction starts and after some induction period the first nuclei of the solid product form. Oxygen ions are removed from the lattice by reduction, and when the concentration of vacancies reaches a certain critical value they are annihilated by rearrangement of lattice with the eventual formation of metal nuclei [33].

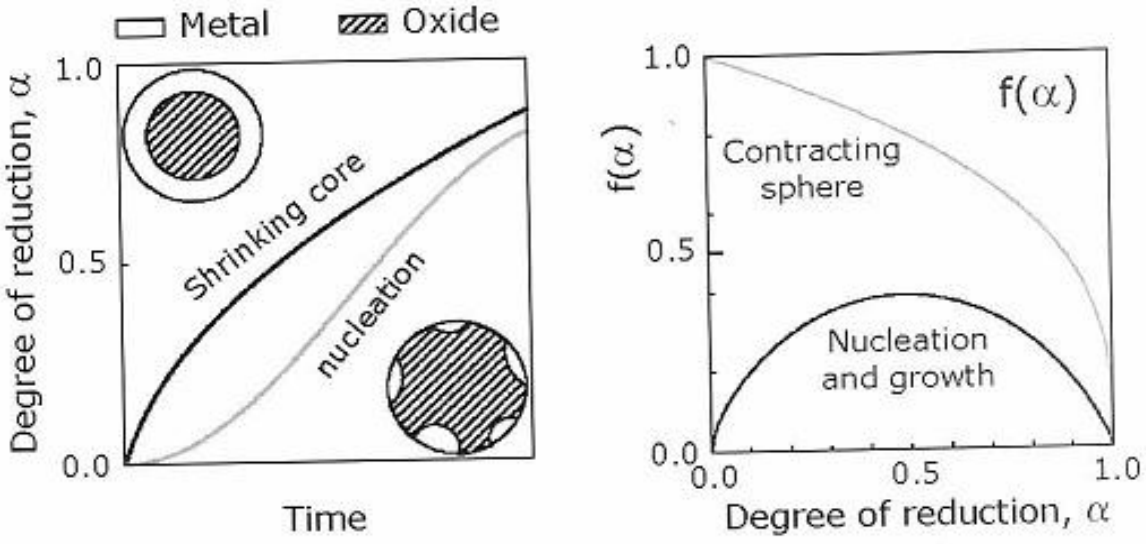


**Figure 2.11: Reduction models and Degree of reduction**

***Left*: reduction models. In the shrinking core or contracting sphere model the rate of reduction is initially fast and decreases progressively due to diffusion limitations. The nucleation model applies when the initial reaction of the oxide with molecular hydrogen is difficult. Once metal nuclei are available for the dissociation of hydrogen, reduction proceeds at a higher rate until the system comes into shrinking core regime. *Right*: the reduction rate depends on the concentration of unreduced sample (1-α) as f(α) [32].**

The reaction interface, which may be visualized as the interface between the nuclei of the metal and the metal oxide, begins to increase more and more rapidly by two processes: the growth of the nuclei already formed and the appearance of new ones. Oxygen ion may be removed by inward diffusion of hydrogen of oxygen ions from the metal/metal oxide interface or outward diffusion of oxygen ions from the metal oxide to the metal/gas interface. At a certain stage of the reduction the metal nuclei have grown at the surface of the oxide grains to such an extent that they begin to make contact with each other. From this moment a decrease of the reaction interface begins because of the overlapping of the metal nuclei and the steady consumption of the oxide grains. These processes continue until the oxide is completely reduced to the metal. The extent of reduction sketched in Figure 2.11(left), after an induction period, increases rapidly and slows down again when reduction gets into the shrinking core regime.

The theoretical treatment of the TPR process as given Hurst et al. [34] and by Wimmers et al. [35] is followed here. Formally, one can write the rate expression for the reduction reaction as eq.(5),

$$MO_n + nH_2 \longrightarrow M_1 + nH_2O \text{----------(5)}$$

under conditions where reverse reaction from metal to oxide can be ignored, as

$$-\frac{d[MO_n]}{dt} = k_{red}[H_2]^p f([MO_n]) \text{----------(6)}$$

in which $[MO_n]$ is the concentration of the metal oxide

$[H_2]$ is the concentration of the hydrogen gas

$k_{red}$ is the rate constant of the reduction reaction

$p$ is the order of the reaction in hydrogen gas

$f$ is the function which describes the dependence of the rate of reduction on the concentration of metal oxide

$t$ is the time

If we write α for the degree of reduction, assuming that the reaction is done in excess hydrogen ($p$=0), using the fact that the temperature increases linearly in time (d$T$=βd$t$) and replacing $k_{red}$ by the Arrhenius equation, we see the temperature dependence of the reduction process:

$$\frac{d\alpha}{dT} = \frac{\nu}{\beta}\exp\left(-\frac{E_{red}}{RT}\right).f(1-\alpha) \text{----------(7)}$$

in which

α is the fraction of reduced material

$f$(1-α) is the function of the fraction of unreduced material

$\nu$ is the pre-exponential factor

β is the heating rate, $\frac{dT}{dt}$

$E_{red}$ is the activation energy of the reduction reaction

$R$ is the gas constant

$T$ is the temperature

The function $f$(1-α) depends on the model that describes the reduction process. The simplest choices would be $f$(1-α)= (1-α) or $(1-\alpha)^q$, as in the review of Hurst et al.[34]. More realistic expressions are those for the nucleation and the contracting sphere models of Fig. 2.11:

These functions are shown in Fig. 2.11 (right).

$f(\alpha) = 3(1-\alpha)^{1/3}$ *contracting sphere*

$f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{2/3}$ *nucleation and growth*

The activation energy of the reduction can be estimated from the temperature $T_{max}$ at which the reduction rate is a maximum by using the following equation (valid under the assumption that both $f(1-\alpha)$ and $\alpha(T_{max})$ do not depend on the heating rate [35,36]:

$$\ln\left(\frac{\beta}{T_{max}^2}\right) = -\frac{E_{red}}{RT_{max}} + \ln\left(\frac{vR}{E_{red}}\right) + \text{constant} \text{----------(8)}$$

The way to use equation (8) is to record a series of TPR patterns at different heating rates and plot the left hand side of (8) against $1/T_{max}$ . The plot should give a straight line with slope $-E_{red}/R$.

### ii) Supported oxides

Metal oxides supported on inert carriers such as $\gamma$-$Al_2O_3$ and $SiO_2$ may exhibit different reduction behaviors compared with the unsupported oxides. Reduction may be of the oxide/supported oxides. Reduction may be hindered or promoted, depending on the nature of the oxide/supported interaction.

Supported metal oxides may be homogeneously distributed across the surface of the support or exist as islands of oxide separated by uncovered support. Islands of metal oxides may be expected to reduce in a similar manner to unsupported oxide, in which case the support may act purely as a dispersing agent and promote the reduction. The concept of a contracting sphere would seem to be inappropriate in the case of a homogeneously distributed supported oxide, so that the reduction may involve instantaneous nucleation across the whole area of the supported oxide.

Metal atoms and crystallites are known to be mobile on the surface of supported metal oxides [37] so that under appropriate conditions the reduction of an homogeneously supported metal oxide may proceed with the reduction of individual metal ions, or groups of metal ions, followed by surface diffusion to form metal crystallites which in turn may diffuse and combine to form particles of the reduced phase. Such a reduced phase may have an autocatalytic effect on the reduction.

The nucleation processes may, however, be hindered by metal supported interactions reducing the mobility of metal atoms. Furthermore, any auto catalytic effect of the reduced phase may be hindered if activated hydrogen species are not mobile across the support surface at the reduction temperature. Hydrogen atoms are known to spill over from supported Pt onto an $Al_2O_3$ only above 600K [38].

### iii) Bimetallic

The promoting influences of foreign metal species on the reduction of bulk oxides are described in this section. For convenience the term “dopant” is used here to signify the foreign metal species added to the bulk oxide.

A dopant may promote reduction either by lowering the activation energy of the rate-determining step or by increasing “pre-exponential” terms. The activation energy for the reduction of CuO was not significantly altered by the addition of Pd or Pt [39], although a strong promoting effect was observed.

Accordingly, the promoting effect of metal dopants would seem to arise from increases in the “pre-exponential” terms. These can be produced in two ways: either by directly increasing the number of nucleation or potential nucleation sites or by

providing a high concentration of active hydrogen that is efficient at causing nucleation. These two methods amount, directly or indirectly, to promotion of the nucleation stages of reduction.

For a doped metal oxide it has been suggested [40] that nucleation can occur at four different types of site:

i) Undisturbed portions of the surface. This is natural or spontaneous nucleation and would correspond to a similar mechanism on untreated samples.

ii) Disorganized portions of the surface, i.e., portions that have been perturbed by the incorporating process, but where no dopant is present.

iii) Portion where the parent metal ion has been replaced by the dopant ion.

iv) Portion where the dopant, representing a distinct new phase is in contact with the metal oxide.

For iii and iv, nucleation occurs in contact with the dopant ion, and the ease of reducibility of the dopant ion, compared to the parent ion, is also important. If the dopant ion reduces first, it may produce a high concentration of active hydrogen on the surface that may promote the reduction.

Reduction is called autocatalytic when reduced metal formed in the early stages of reduction catalyzes the reduction by $H_2$ activation. It would appear in these examples that the role of the dopant is that of hydrogen activator, i.e., the nucleation steps are indirectly promoted. If the dopant is incorporated into the lattice, it may activate hydrogen that can diffuse by intra-particular spillover. This process may be expected to be very efficient. However, if the dopant exists as a distinct phase, then the hydrogen must diffuse by the less efficient intra-particular spillover mechanism. This can greatly affect the promoting influence of a metal on the reduction of an oxide [39].

First row transition metals (Cr, Mn, fe, Co, Ni) have also been found to promote the reduction of CuO [39]. In such cases the dopant ion is not thought to reduce before the parent ion, and the promoting effect is thought to arise due to increased nucleation at sites such as ii and iii above.

Indeed oxides which reduce by a contracting sphere model when undoped cannot have their reductions promoted [40], e.g., the reduction of $MnO_2$ to Mn metal, which is characterized by a continuously decreasing rate, is not promoted by the presence of many substances ( Ti, Cr, w, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Cu, Ag). It would appear that the undoped oxide reduces by a spontaneous nucleation over the entire surface immediately on contact with hydrogen, and the presence of a dopant metal is unable to promote the reduction by either nucleation or hydrogen activation.

## *2.4 TPR STUDIES FOR SUPPORTED CATALYSTS*

Most work on the characterization of materials using TPR has been carried out in relation to catalysts and predominantly on supported metal catalysts in the oxidic form. Supported catalysts often have very high metal dispersions and low concentrations of active catalytic components. That is why it is difficult to characterize such catalysts by conventional methods.

Shakeel Ahmed, K. Alam and T. Inui studied hydrogen spillover effect in hydro-cracking catalyst in 2002 [41]. Temperature-programmed reduction (TPR) was used to study the hydrogen spillover effect. The phenomenon is defined as the dissociative chemisorption or adsorption of hydrogen on the metal and migration of atomic hydrogen to the surface of the support such as alumina, silica, and zeolites.

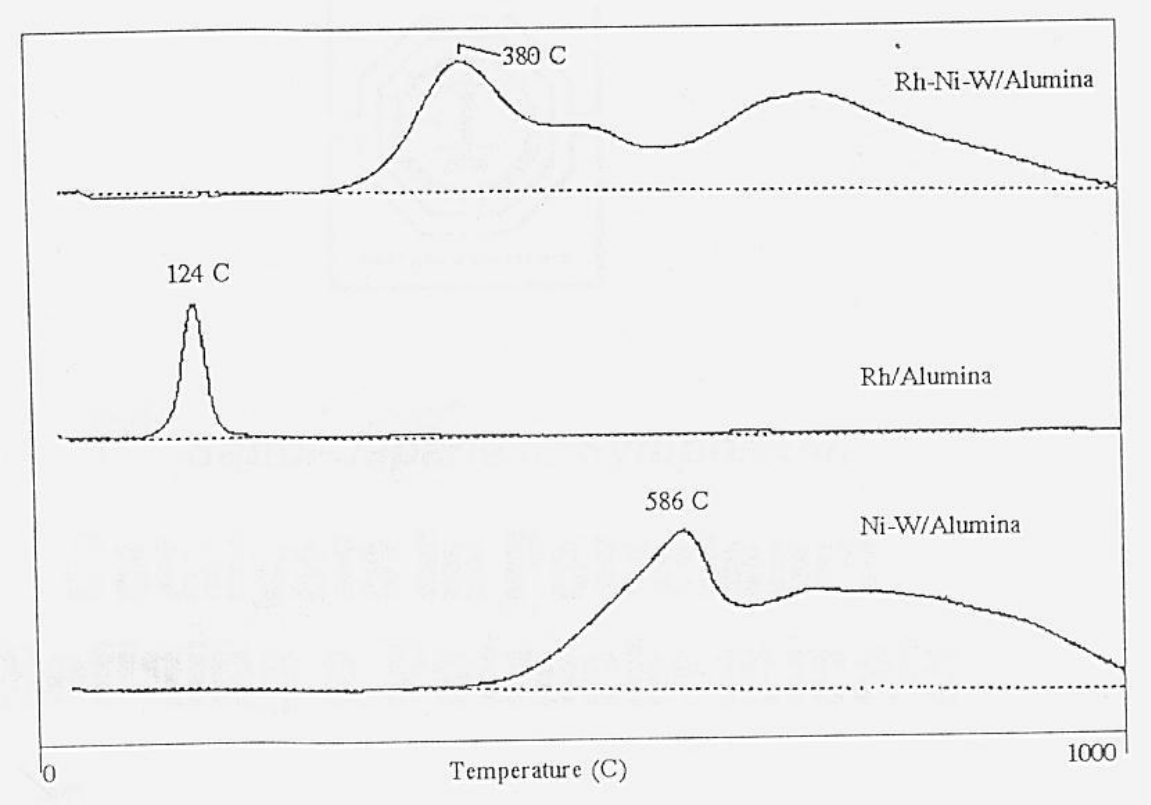


**Figure 2.12: TPR profiles of metal supported alumina catalysts.**

The authors established a novel method to incorporate a very small amount of precious metal directly on the base metals supported catalyst to enhance the hydrogenation functionality. Figure 2.12 shows the TPR profile.

A marked reduction in the peak temperature was observed by incorporation of precious metal in a relatively small amount. Figure 2.12 shows the results of TPR experiments. Ni-W supported on alumina reduced at around 586°C. This substantial reduction by a novel method produced a large reduction peak at 380°C. This substantial reduction in peak temperature is a clear indication of the hydrogen spillover effect. It is beneficial to reduce the amount of expensive noble metals in catalysts. The effect was observed with a relatively very small amount of Rh. On the other hand, the authors saw that with conventional methods of impregnation, 2 wt.% Rh was loaded on alumina TPR results showed a small peak at 353°C. A large peak at 125°C for Rh, may be present on the surface as un-reacted, and main peak around 573°C for base metals were observed.

Therefore, from the above results we can conclude that TPR can explain the cause of increased activity.

### 2.4.1 Monometallic

Dispersed $Pt/Al_2O_3$ is extensively used as a catalyst, especially in the reforming process. Treatments in oxygen and in hydrogen are established procedures in the activation of fresh catalyst as well as in the regeneration of spent catalysts. Usually catalysts with a range of 0.3% to 0.6% platinum are used. These are prepared by impregnation of alumina with platinum metal salt ($H_2PtCl_6$), drying in air at 393K,

calcined at 773 k and finally reduced in $H_2$ at 773K. Therefore, to obtain a well-dispersed catalyst, primary attention to the pretreatment steps of drying, calcinations and reduction must be given.

Lieske et al [42] studied the formation of oxidized Pt species during treatments in oxygen at different temperatures using TPR. Two oxides α and β-[PtO2]s and two chloride-containing surface complexes of $[Pt^{iv}O_xCl_y]$s, that could act as a re-dispersing agents were found. This is supported by the fact that the temperature range where the agents can be formed is the same as the known temperature of re-dispersion approximately 773 to 873 K.

They proposed that the TPR peak was due to reduction of Pt-O-Cl containing surface complex stabilized by interaction with $Al_2O_3$. The authors showed in fact that a Cl-dispersal step is essential in the regeneration of Pt/ $Al_2O_3$ catalysts. Similarly, Blanchard et al. [43] using TPR, found in a $Pt/Al_2O_3$ catalyst that the interaction between the Pt Particles and alumina support came during the drying step.

From the results, it can be said that the TPR techniques enables the fine differences between catalysts prepared by different methods to be established. TPR provides a method for studying the optimum parameters for calcinations/ reduction treatments.

In another study, Pd supported on $TiO_2$, $Al_2O_3$, $SiO_2$ and carbon was chosen as a system [44]. Palladium differs from other metal catalysts in its interaction with hydrogen because in addition to chemisorptions, it absorbs hydrogen into the bulk [45]. This adsorption interferes with the chemisorptions and may cause an error in the determination of the dispersion of palladium catalysts. Pd was found to reduce at

temperatures lower than 473 K. Spillover of hydrogen from Pd to supports occurred at higher temperatures. Hydrogen treatment at higher temperature can also induce strong metal support interactions (SMSI) and sintering. It was found that under the same reduction conditions, the sintering of supported palladium catalysts follows the trend $Pd/C>Pd/TiO_2>Pd/Al_2O_3>Pd/SiO_2$.

TPR was able to demonstrate how the rate of sintering of the Pd metal could be related with the support employed.

In the past 20 years Rh has been gaining importance in catalytic chemistry. Not only is Rh widely recognized as the best catalyst to promote the reduction of NO in three way catalysts, but also takes a special place in the conversion is synthesis gas, since its product-range can comprise oxygenated products as well as hydrocarbons. Supports are often impregnated or exchanged with metal chloro-complexes. To give an idea of the chloride evolution on supported rhodium precursors the TPR was studied by Marques da Cruz et al. [46]. Hydrogen-oxygen titration and specific rate as well as turnover frequency have shown that total reduction may occur at relatively low temperatures and without total dechlorination. Strong interactions between support and metallic complex control the initial and final temperatures of reduction and dechlorination.

Vis et al. [47] studied supported $Rh/Al_2O_3$ and $Rh/TiO_2$ catalysts with varying metal loadings by TPR and TPO and hydrogen chemisorptions. TPR/TPO showed that well dispersion of Rh on $Al_2O_3$ was due to the growth of two different kinds of $Rh/Rh_2O_3$ particles on $TiO_2$; one kind was easily reduced /oxidized, with a high dispersion. In is seems that in this study of catalyst varying metal loading, the

temperature programmed reduction technique was able to demonstrate how the reduction properties of metal could be related to the dispersion of the metal.

Temperature programmed reduction experiments on copper on titania- and silica supported catalyst were studied by Delk et al. [48]. The results are shown in the Figure 2.13, in which the most obvious and significant difference is the lower reduction temperature of the titania-supported copper. Both the 1% and 4% cu/$TiO_2$ show reduction peaks at 403 K. There is a second peak at 493 K in the 4% Cu/$TiO_2$. In the 1% Cu/$TiO_2$ there is a shoulder at the same temperature. In the case of silica supported copper, the reduction peaks are found at 541 K and 502 K for the 4% and 1% Cu/$SiO_2$ samples, respectively. The 1% Cu/$SiO_2$ also displays a shoulder at 548 K. The higher temperature peak arises from reduction of $Cu^{+2}$ species that are not in such close contact with the support. An interesting feature is consumption of hydrogen at temperature above 573K, after all the Cu is reduced. This was interpreted as being due to the reduction of the titania support catalyzed by copper metal.

Temperature programmed reduction studies suggest that there is an anomalous copper-support interaction involved by high temperature reduction.

The wide range of application of supported nickel catalysts in hydrogenation and various stabilization and hydro-treating processes has been the reason for a great deal of studies aimed at their activity and selectivity. TPR on Ni/$SiO_2$ catalysts showed that the amount of Ni in strong interaction with the silica increased with decreasing loading and increasing calcinations temperatures. This suggests that a chemical rather than a transport effect is dominant. The influence of calcinations can be shown in Figure 2.14, in which as calcinations temperature increased the reduction becomes more difficult and metal particles of reduced species were smaller.

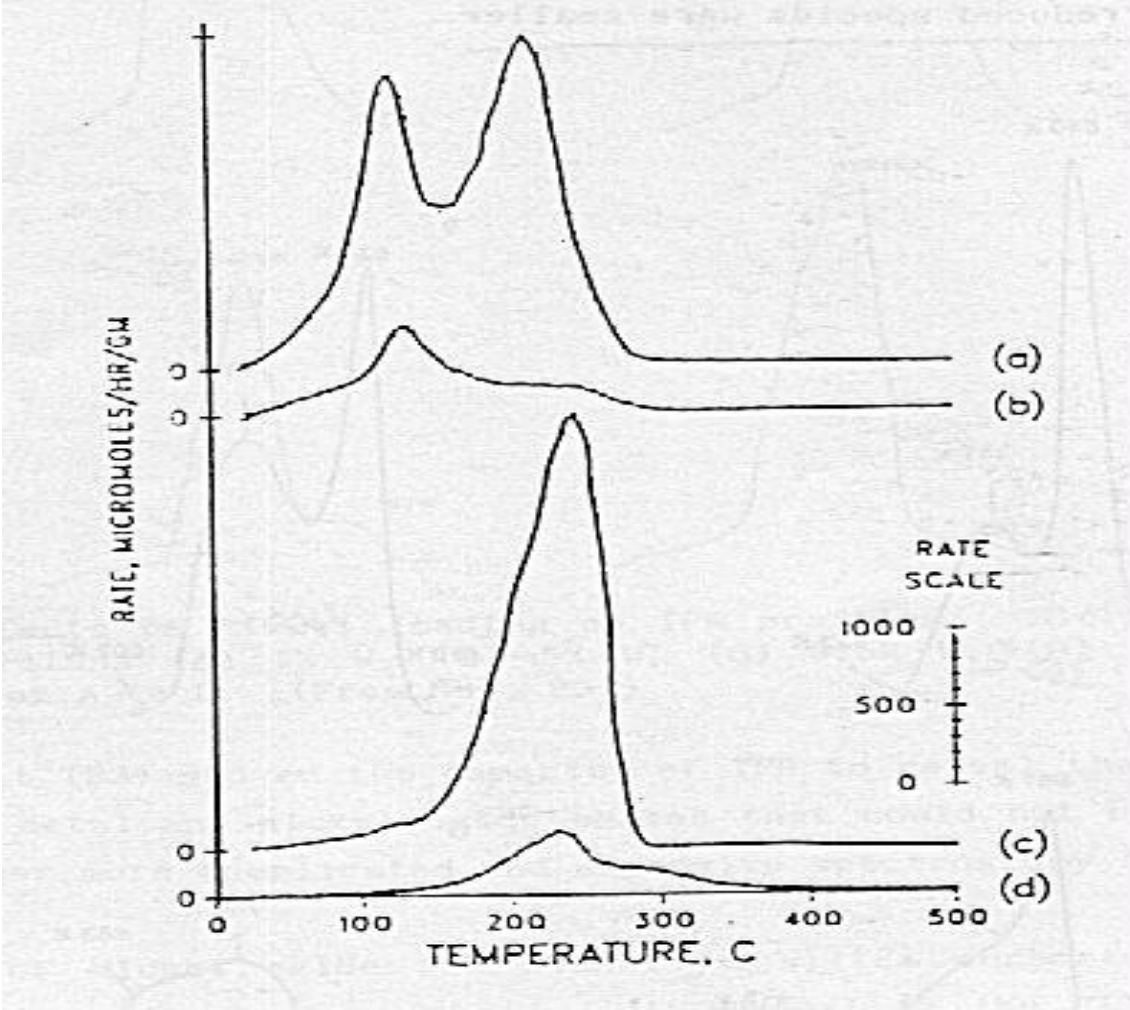


**Figure 2.13: Temperature-programmed reduction of supported copper catalysts following calcinations at $450^0$C (a) 4% $Cu/TiO_2$, (b)1% $Cu/TiO_2$, (c) 4% $Cu/SiO_2$, (d)1% $Cu/SiO_2$ [48].**

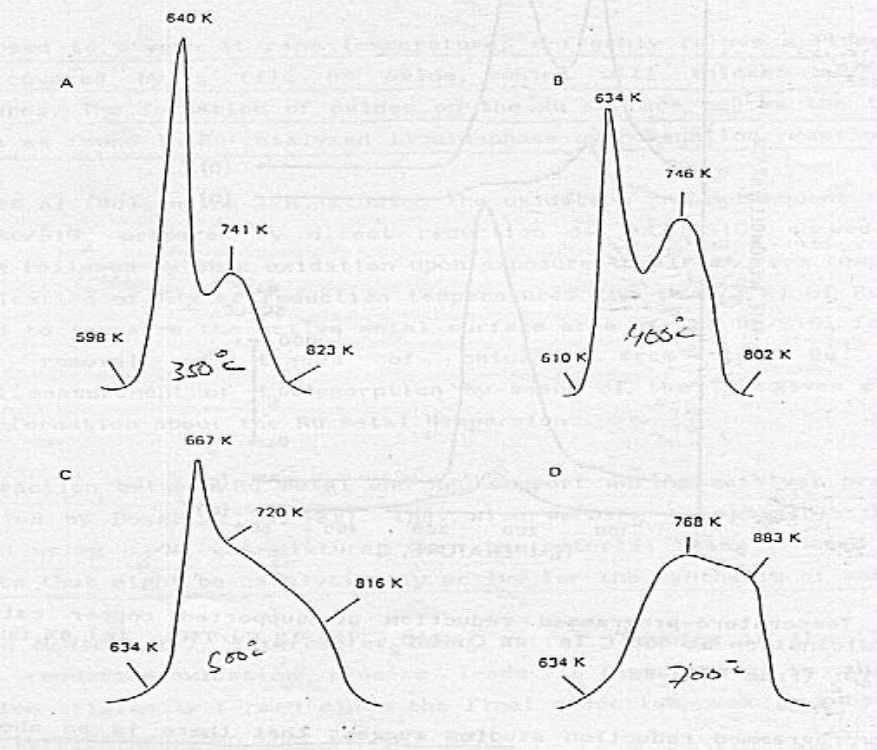


**Figure 2.14: Effects of calcinations temperature on TPR profile of 1%nickel on micronized Gasil 35 silica.**

**(A) 623 K, (B) 673 K, (C) 773 K, (D) 973 K [49].**

Furthermore, increase in the metal loading led to an increased population of Ni arising from the low temperature reduction peaks and as a consequence larger Ni particle sizes, as can be seen in Figure 2.15. Reducibility of Ni on $\gamma$-$Al_2O_3$ is much more difficult than on silica [49]. The interaction of Ni with $Al_2O_3$ is clearly much stronger than the interaction that occurs with silica.

Mile and Zammit [49] showed the capacity of TPR to reveal the characteristics of the nickel metal and nickel oxide phases that could not be able to detect by using another more complicated and expensive spectroscopy technique.

The location of Nickel oxide and nickel in silica-supported catalysts was studied by Mile et al. [50]. As shown in Figure 2.16 the TPR of bulk nickel oxide consisted of a single reduction peak at 673 K slightly skewed toward lower temperatures. At 523 K the peak was found to be small. Supported nickel on silica shows the marked effect of the support in producing a number of peaks and broadening the whole profile to much higher temperatures. There are three reduction peaks at 523, 673, and 773 K and a chemisorptions peak at 533 K obtained on cooling the sample from 873 K to ambient in the $N_2/H_2$ carrier gas stream.

In conclusion the authors were able to distinguish two different types of NiO using TPR with temperature difference ~100 K, with the more reducible oxide is located mainly in the small pores and the less reducible oxide located in the large pores.

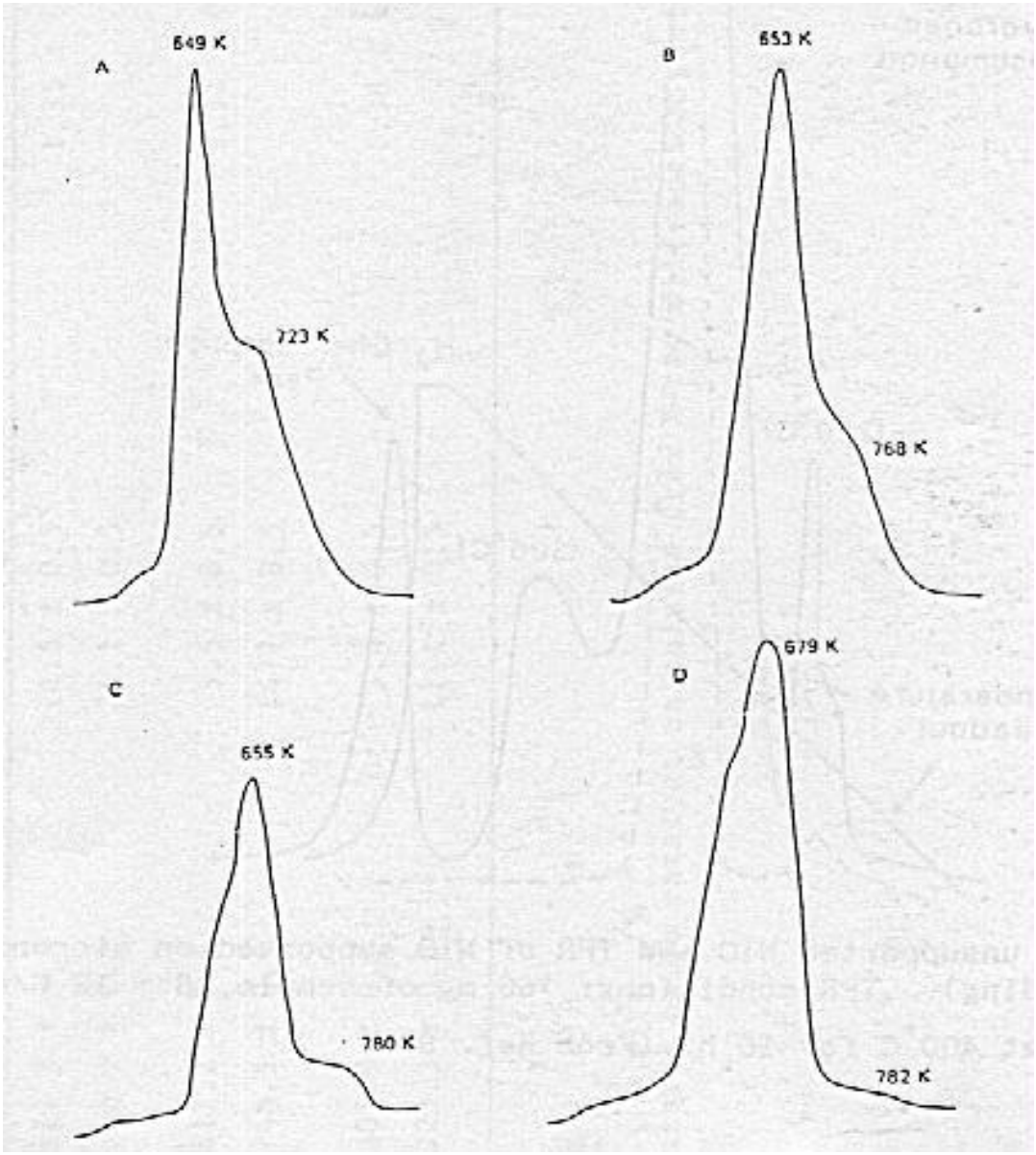


**Figure 2.15: Effects of nickel loading on TPR profiles.**

**Micronized Gasil 35. Standard conditions (A) 1% W, (B) 5% W, (C) 9.5% W, (D) 31% W. Reduced sensitivity from A to D. [49].**

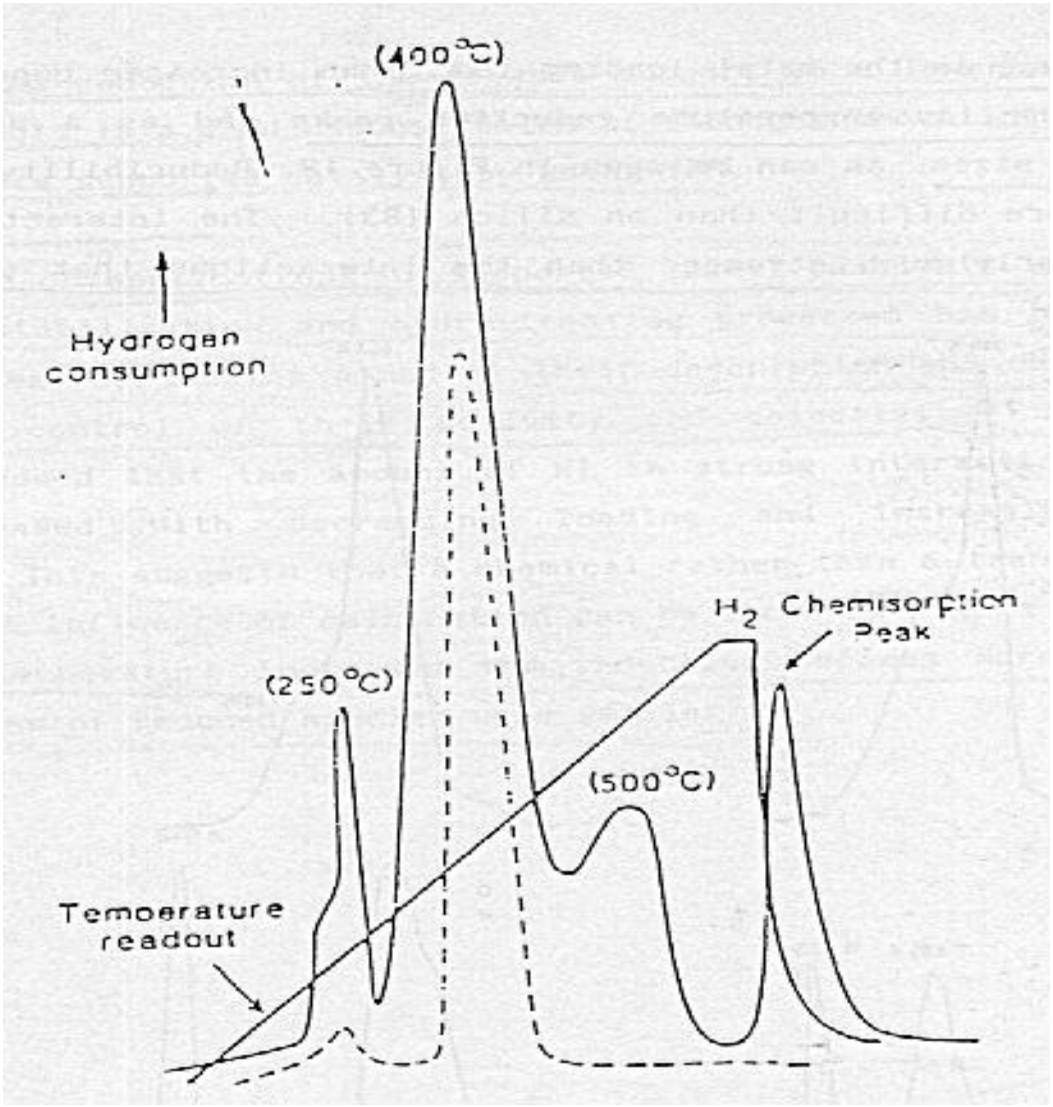


**Figure 2.16: TPR of unsupported NiO and TPR of NiO supported on micronized Gasil 35 (8.8% (w/w) loading).**

**Conditions: 60 mg of sample,β=12$^0$C/min, 5%$H_2$-$N_2$calcination at 400$^0$C for 16 hr [50].**

Rhenium catalysts have several interesting properties. They show high activity for metathesis, hydrodesulphurization and hydrodenitrification. It is known that Re also increases the stability of Pt reforming catalysts.

Detailed information on reducibility as such, is important because catalytically active re sites are only created by reduction of the $Re^{+7}$ ions, generally present in freshly prepared catalysts, to lower valencies as is the case when Re carbines and $ReS_2$/Re metal are formed.

In an interesting work, TPR has been applied to characterize the reducibility of $Re_2O_7$ supported on $Al_2O_3$, $SiO_2$ and carbon catalysts [51]. Figure 2.17 shows the TPR patterns of dried $Al_2O_3$- supported catalysts as a function of Re content. At low Re contents, the TPR patterns are dominated by peaks which are not related to reduction of Re ions. Differences in the concentration of additives such as chloride might explain these variations. A peak near 1100 K is found assigned to reduction of $Al_2O_3$ impurities, such as iron, sulfide and sulfate. The latter causes a 200 K fall in for a higher Re content, suggesting that this reduction is catalyzed by Re.

Figure 2.17 also showed the TPR patterns of dried $SiO_2$ – supported catalysts as a function of the Re content. Besides $Re^{+7}$ reduction, a reduction pattern is observed between 800 K and 1200 k, which is typical for the $SiO_2$ support. As in the $Al_2O_3$ case, it is assigned to the reduction of impurities. Again, one can conclude that Re catalyzes this reduction, since its presence causes the appearance of a second maximum in the $SiO_2$ reduction pattern as well as shift to lower reduction temperatures.

The pattern of dried carbon-supported catalysts as a function of Re content is also presented in Figure 2.17 for comparison. The reduction peaks are small compared with those caused by gasification of the support, occurring in the region of 500-1240K.

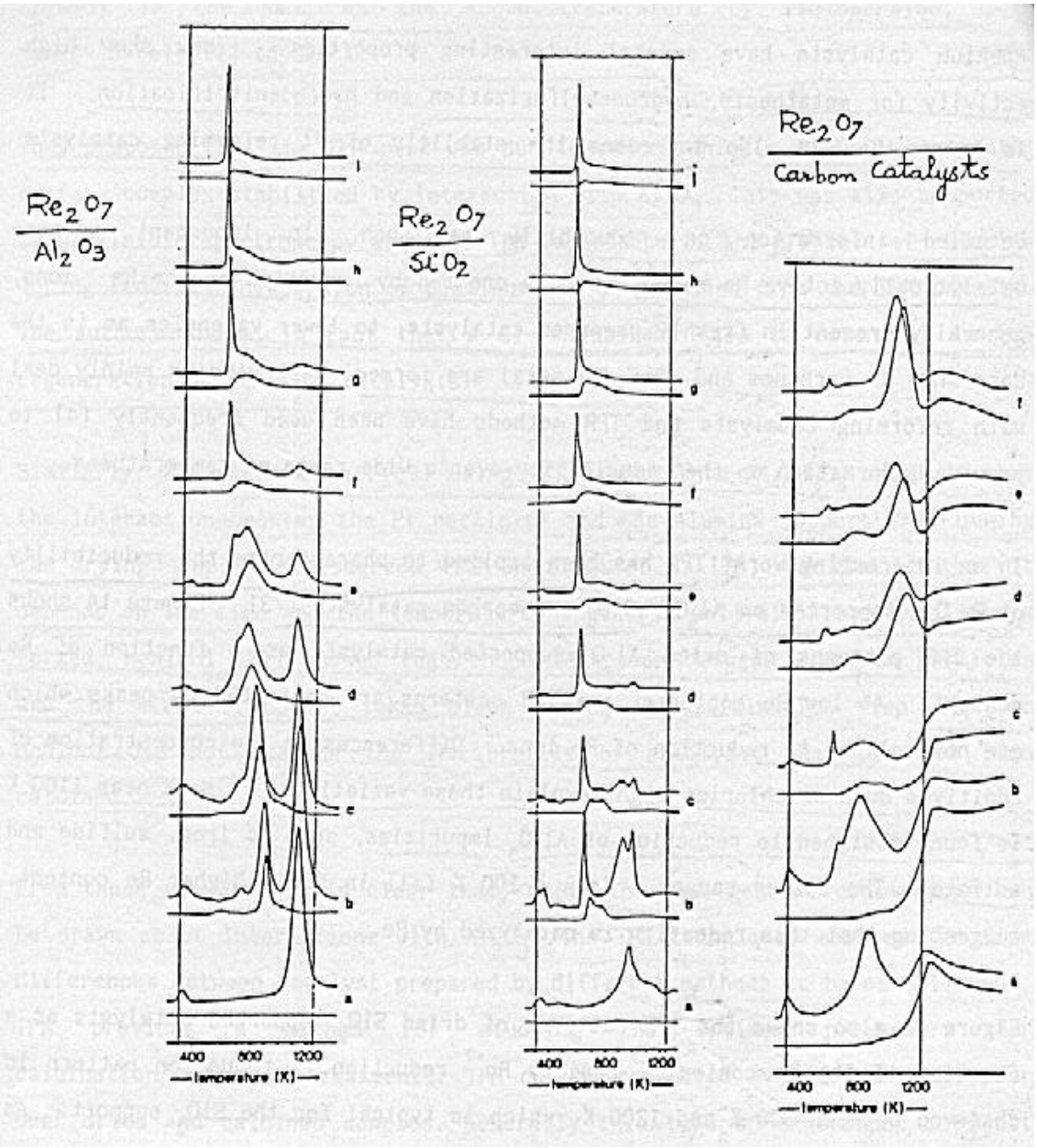


**Figure 2.17: TPR patterns (10 K/min) of dried $Re_2O_7$/ $Al_2O_3$, $Re_2O_7$/ $SiO_2$ and $Re_2O_7$/ carbon catalysts having the following Re contents (at./nm$^2$): (a) 0, (b) 0.0080, (c) 0.040, (d) 0.20, (e) 0.38,(f) 0.80. The upper and lower part of each pattern represents the TCD and FID signals, respectively. [51]**

In general it can be seen that dried catalysts are found to contain a so-called monolayer-type $Re^{+7}$ surface phase as well as crystalline $NH_4ReO_4$. With respect to the reduction of $NH_4ReO_4$ crystallites TPR has advantages over other techniques (such as XRD), because TPR can be used for quantitative analysis and for detection of the very small metal clusters.

Calcinations at 575 k or 825 K resulted in decomposition of the Re ammonia salt, formation of the $Re^{+7}$ surface phase and $Re_2O_7$ clusters, and Re loss as a sublimation of $Re_2O_7$.

Differences in reducibility of the various catalysts samples are ascribed to variations in the strength and the heterogeneity of the $Re^{+7}$ support interactions. The strength of the interaction was found to depend on the support material and decreases in the order: $Al_2O_3$> $SiO_2$>carbon. The largely varying literature data on the reducibility of $Re_2O_7$/ $Al_2O_3$ catalysts is supposedly with the presence of additives, such as chloride, which may increase the $Re^{+7}$ support interaction.

From the results of this work it is shown that the TPR technique is given clear evidence on the reducibility of the metal over a wide range of temperature and on the structure of the catalyst, e.g. on the presence of metal clusters and on the metal-oxygen bond strength.

From the different papers reviewed in this section on monometallic supported catalysts we can conclude that the temperature-programmed analysis technique has provided valuable information on the ease of reduction information o the ease of reduction, valency state of metals, metal-support interactions and the influence of one component in the support on the reducibility of another component.

### 2.4.2 Bi-metallic catalysts

For the past 25 years, bimetallic catalysts are a subject of considerable interest in catalyst research because their performance differs markedly from that of their components, and consequently the constitution of supported bimetallic catalysts has been the object of a great deal of work.

In order to understand the catalytic behavior of bimetallic catalysts, the most fundamental question is, whether the catalyst particles indeed contain atoms of both metals. A direct experimental verification is difficult due to the limitation of existing physical techniques.

The temperature programmed reduction and oxidation techniques (TPR-TPO) may however be used to obtain evidence for the interaction between the atoms of the two metallic components.

Tapan K. Das et al. characterize catalytic properties of rhenium promoted cobalt alumina catalysts [52]. They showed that addition of small amounts of rhenium to a 15% $Co/Al_2O_3$ catalyst decreased the reduction temperature of cobalt oxide but the percent dispersion and cluster size, based on the amount of reduced cobalt, did not change significantly.

Figure 2.18 shows the TPR profile for the un-promoted 15% $Co/Al_2O_3$ catalyst in comparison with TPR profiles for promoted catalysts that contain increasing loadings of rhenium.

The low temperature peak (500-650K) is typically assigned to reduction of $Co_3O_4$ to CoO, although a fraction of peak likely corresponds to reduction of the larger, bulk-like CoO species to Co°.

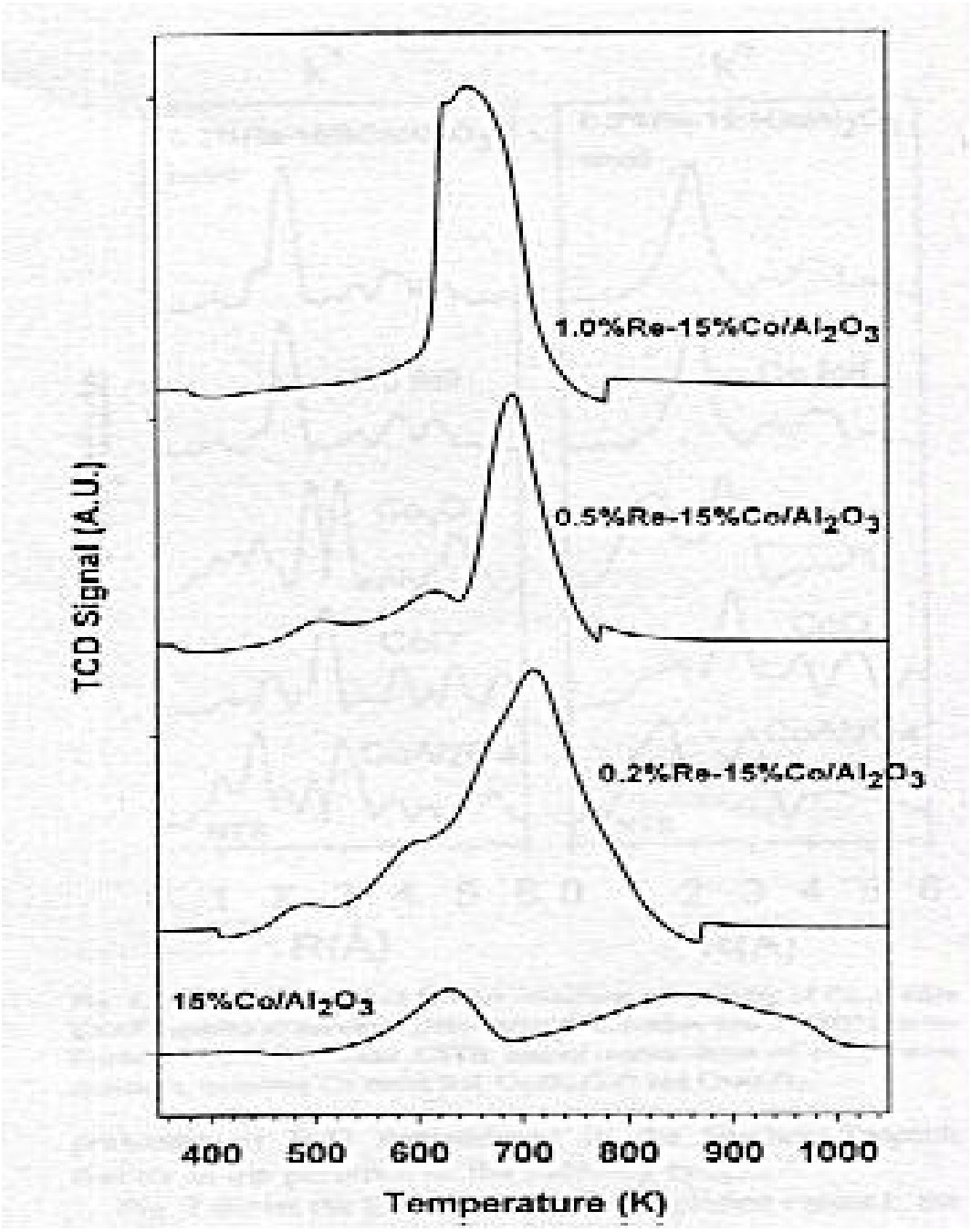


**Figure 2.18: Comparative TPR spectra of un-promoted and rhenium promoted 15% $Co/Al_2O_3$ catalysts.**

The broad peak for unsupported 15% $Co/Al_2O_3$ catalyst (700-1000 K) is attributed to the reduction of cobalt species that interact with the support, and the different shoulders are likely due to varying degrees of interaction that depends on cluster size. The addition of rhenium caused the high temperature peak to shift to a lower temperature (Fig. 2.18), and the shift of this peak to a lower temperature increases with rhenium loadings. Figure 2.18 shows no increase in the extent of reduction for the low temperature peak assigned to the reduction of cobalt oxides to CoO.

A further reduction of CoO appears as a low temperature shoulder on the sharp peak for reduction of the Co surface support species with the addition of Rhenium. A small peak in the TPR profile below 500 K on the 0.2 and 0.5% rhenium containing samples is assigned to the decomposition of a small amount cobalt nitrate that had not decomposed during calcinations. This peak was not seen if the sample calcined at higher temperature.

The authors conclude that small amounts of rhenium added to the cobalt catalyst decreases the reduction temperature of cobalt oxide but did not significantly alter the actual dispersion (and therefore, cluster size), based on the amount of reduced cobalt, to an appreciable amount. Addition of rhenium increases the percent reduction of cobalt and hence initial activity.

Temperature programmed reduction has been used to examine the effect of drying on the reduction of Pt-$Re/Al_2O_3$ catalysts [53]. Drying has little effect on the reduction of the monometallic Pt /$Al_2O_3$ and $Re/Al_2O_3$ as can be seen in Figure 2.19.

Both the number of TPR peaks and the peak maximum temperature of the Pt-Re/ $Al_2O_3$ vary with drying temperature (Fig. 2.19). The TPR profile of Pt-Re/ $Al_2O_3$

catalyst dried at 373 or 573 K consists of a single peak with a peak maximum temperature similar to that of monometallic Pt/ $Al_2O_3$. The size corresponds to the reduction of both Pt and Re. At the other temperature extreme of (773 K) two TPR peaks are found, one at a temperature-characteristic of monometallic Re. They interpreted their results on the fact that water influenced the rate of $Re_2O_7$ migration to Pt centers; the mobility of $Re_2O_7$ and hence, its rate of diffusion to Pt Centers was dependent on drying temperatures.

Low-temperature drying below 273 K does not remove the water adsorbed by the catalyst during storage and the $Re_2O_7$ is still hydrated. The suggestion is that this hydrated $Re_2O_7$ is mobile and is able to migrate to the Pt reduction centers. Thus, the reduction of the two metal oxides is essentially simultaneous, resulting in a single TPR peak, and an alloy is formed. In contrast, high-temperature drying, 773 K, dehydrates the $Re_2O_7$ which is no longer able to migrate to the Pt reduction centers. The $Re_2O_7$ therefore reduces at the temperature of the monometallic $Re/Al_2O_3$ resulting in two TPR peaks and by implications no alloy is formed.

In another work, Wagstaff and Prins [54] used TPR to characterize the finely dispersed metal compound in a series of Pt-$Re/Al_2O_3$ catalysts. Strong evidence has been obtained that zero valent Pt and Re atoms are in intimate contact with each other after catalyst reduction. The formation of bimetallic clusters supports the explanation of alloys causing the improved performance of the bimetallic system. Treatment of the reduced catalyst with oxygen above 473 k causes segregation of platinum-rich species around 273 K and reduction of a rhenium-rich species around 523 K.

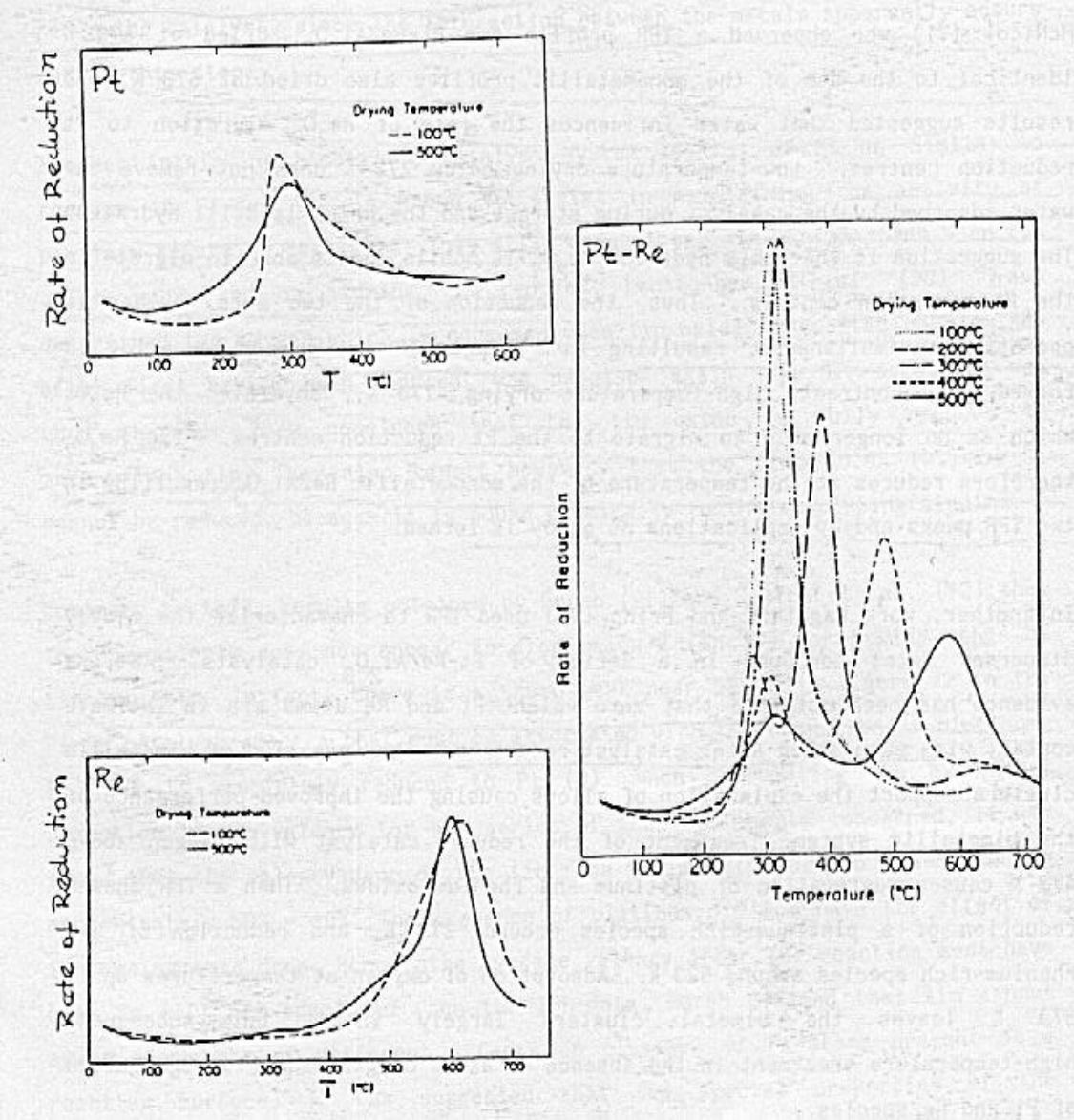


**Figure 2.19: Temperature programmed reduction of Pt/ $Al_2O_3$, Re/ $Al_2O_3$ and Pt/Re/$Al_2O_3$ catalyst. [53]**

Adsorption of oxygen at temperatures up to 373 K leaves the bimetal clusters largely intact but subsequent high-temperature treatment in the absence of extra oxygen leads to segregation of Pt and Re species.

Mieville [55] also observed in TPR that an interaction occurs with Pt and Re when Pt-Re catalysts are preoxidized at 573 K or lower; re-reduced at lower temperatures compared to $Re/Al_2O_3$. At 773 K preoxidation, TPR profiles of Pt-Re show no interaction and are similar to what they would be if superimposed Pt-Re catalysts, previously exhibiting catalytic reduction. Intimate mixture of $Pt/Al_2O_3$ and $Re/Al_2O_3$ particles preoxidized at 573 k, also exhibit reductive interaction; however, loose mixture of relatively large particles does not. The explanation could be that $H_2$ spillover initiates Re oxide reduction by creating nuclei of Re, which then catalyze the reduction of the remaining oxide. The overall mechanism is controlled by the rate of spillover that in turn is determined by the degree of hydration of the alumina surface.

The implication of TPR results from the above results is, that the reduction step is of critical importance in the preparation and regeneration of Pt-Re reforming catalyst, since the interaction between the metals apparently occurs during this step.

A new system used in catalytic reforming is $Pt\text{-}Ge/Al_2O_3$ catalysts. Again here, the main question arises as to the real nature of the interaction between the metals in this catalyst.

Goldwasser et al. [56] studied two series of $Pt\text{-}Ge/Al_2O_3$ catalysts that were prepared using different calcinations procedures. Both series were calcined prior to the addition of platinum at 873 K. The TPR showed that there was complete reduction of Pt(IV) to Pt(0) for all catalysts and partial reduction of the germanium(IV) precursor in the case of high loading germanium catalysts for series only calcined at 673 K. The

results (calcinations prior to the addition of Pt at 873 K) indicate that germanium, after calcinations at 873 K is stabilized in the alumina support in such a way that its reduction does not occur under TPR conditions; there is no catalytic effect in respect of the reduction of germanium(IV) by the metallic platinum. Evidently, a dilution or geometric effect would be almost impossible under these conditions.

De Miguel et al. [57] using TPR, showed that calcined Pt-Ge/$Al_2O_3$ would contain approximately 40-50% Ge(0) after reduction at 1073 K, unlike the Ge/$Al_2O_3$ catalyst, where Ge was not reduced to the zero-valent state; it can be inferred that a fraction of Ge would be reduced to Ge(0) below 723 K in Pt-Ge/$Al_2O_3$ catalysts. Assuming that Ge(IV) could be reduced only to the zero-valent state up to 723 K in bimetallic catalysts, the percentage of Ge(0) calculated was approximately 25% of the total Ge content.

The results of TPR profiles of bimetallic samples (below 723 K) show both a broadening of the first reduction peak and an intermediate reduction zone would indicate a certain catalytic effect of Pt on the Ge reduction. It is clear that in bimetallic reforming catalysts, the TPR profile is a useful indicator of catalyst conditions in the calcined and reduced state. This is important for the study of the re-dispersion process of the catalyst TPR, and then could be applied as a fairly rapid, reliable and cheap technique for the study of a particular catalyst preparation process.

It is known that Mo-based hydro-treating catalysts are used in the oil industry for the removal of organo-sulfur and organo-nitrogen contaminants.

Burch and Collins [58] studied Ni-Mo/$Al_2O_3$ catalysts containing different concentrations of Ni and Mo prepared by wet impregnation. The TPR of sulfided Ni-

Mo catalysts has shown that the promoted catalysts behave differently from either Ni or Mo catalysts.

Furthermore they [58,59] studied a series of industrial catalysts, using TPR, to obtain information on the behavior of these catalysts before and after regeneration. Figure 2.20 shows the different TPR profiles of used and fresh catalysts.

The fresh catalyst has a peak maximum at 487°C and shoulder at 527°C, whereas the regenerated catalyst has a peak at 557°C and a shoulder at 547°C. It is shown that the regenerated catalyst has become more difficult to reduce at low temperatures. However, the long tail for the fresh catalyst at high temperatures is less apparent for the regenerated catalyst that could indicate a decrease in the amount of highly dispersed Mo present. The decrease in the case of reduction after regeneration is consistent with the lower surface area and the lower HDS activity for this catalyst. From this paper it is important to conclude that TPR can provide a quick and easy way of checking the effect of regeneration on the HDS catalysts.

Van't Blik and Prins[60,61] studied the effect of support on bimetallic Co-Rh catalyst using TPR techniques. They conclude:

- On Co-Rh/$Al_2O_3$ catalyst, TPR showed a reduction peak at a much lower temperature than that of Co/$Al_2O_3$. This and the slight shift relative to the peak of Rh/$Al_2O_3$ indicate that cobalt and rhodium ions are far apart after co-impregnation. This explains why bimetallic particles are easily formed during reduction. Oxidation at room temperature of the bimetallic particles largely intact; but cobalt is oxidized to a large extent while rhodium remains metallic. TPR analysis of these catalysts also suggested that in the reduced state the bimetallic particles are already surface-enriched in cobalt.

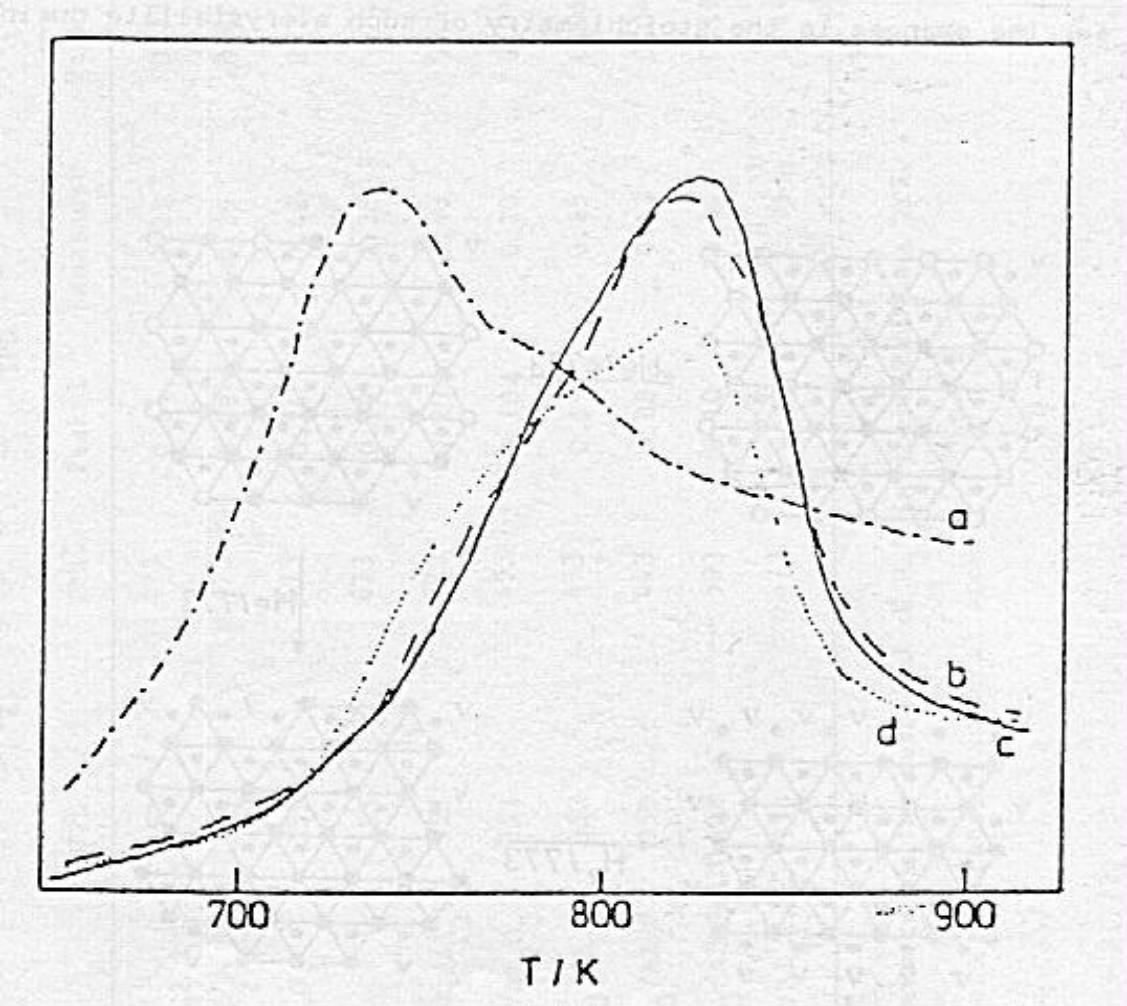


**Figure 2.20: TPR profiles for regeneration catalysts**

**(a)Fresh catalysts, (b) and (c) repeat TPRs on two samples from the same batch of regenerated catalyst, (d) regenerated catalyst after heating for a further 40 h at 723 K. [59].**

- On Co-Rh/$TiO_2$, the addition of rhodium to cobalt caused the resulting bimetallic catalyst to be more difficult to oxidize, while the reducibility of the catalyst depends on the oxidation temperature. When oxidized below 800 K, the reduction proceeded at low temperatures, indicating that $Rh_2O_3$ was present in the surface of the bimetallic particles. To complete the oxidation, however, higher temperatures were needed and under these circumstances cobalt rhodate, $CoRh_2O_4$, was formed. The TPR reduction behavior of a oxidized catalyst reveals that only cobalt oxide was exposed, demonstrating the oxygen-induced surface enrichment by cobalt.

- On Co-Rh/$SiO_2$ catalysts, the reduction proceeds at lower temperatures than the reduction of Co/$SiO_2$ catalysts, indicating that Rh catalyzes the reduction of the cobalt metal salt and cobalt oxide.

From these studies become clear that TPR is able to supply useful information about the structure of the reduced bimetallic Co-Rh supported on different carriers.

## *2.5 INFLUENCE OF EXPERIMENTAL PARAMETERS*

It is known, both experimentally and from calculations, that the position and shape of a TPR profile are influenced by the heating rate, the flow rate of the reducing mixture, the concentration of hydrogen in the latter, and the amount of oxidic material subject to reduction.

The effects of the support type, preparation method, metal loading on catalyst properties were studied by Afzar Hasan et al. [62]. They found significant differences in properties dependent on the preparation method and type of support used. From TPR experiment they found a relationship between the reducibility of oxidic precursors and

the hydrogenation activity of the sulfided catalysts. They concluded that the higher the reducibility, the higher the hydrogenation activity. Catalyst prepared on mixed supports gave higher amounts of saturates.

G. Munteanu and M. Craiu studied [63] the influence of the experimental parameters. They varied heating rate, the flow rate of the reducing mixture and the hydrogen concentration in this mixture, and amount of NiO, the granularity and the concentration of NiO in the reaction space.

Figure 2.21a shows the dependence of the TPR peak position on the flow rate, both for constant pressure and for the case in which the pressure varies together with the flow rate, as in Figure 2.21b.

By comparing the two curves of Fig. 2.20a, the conclusion drawn is that the effect of reactor pressure variation is greater than that of corresponding flow rate variation. This conclusion is also confirmed by the results illustrated in Fig.2.20b.

The effect of variation of amount of NiO(Fig. 2.20-c) increases when the hydrogen concentration decreases. A similar effect can be noticed when the reactor pressure decreases. These effects should be expected, since both the hydrogen concentration in the reducing mixture and the pressure in the reactor can lead to the decrease of hydrogen concentration in the reactor space.

Considering all these results, one can conclude that lowering the pressure in the reaction space could increase the resolution and even the sensitivity of the method.

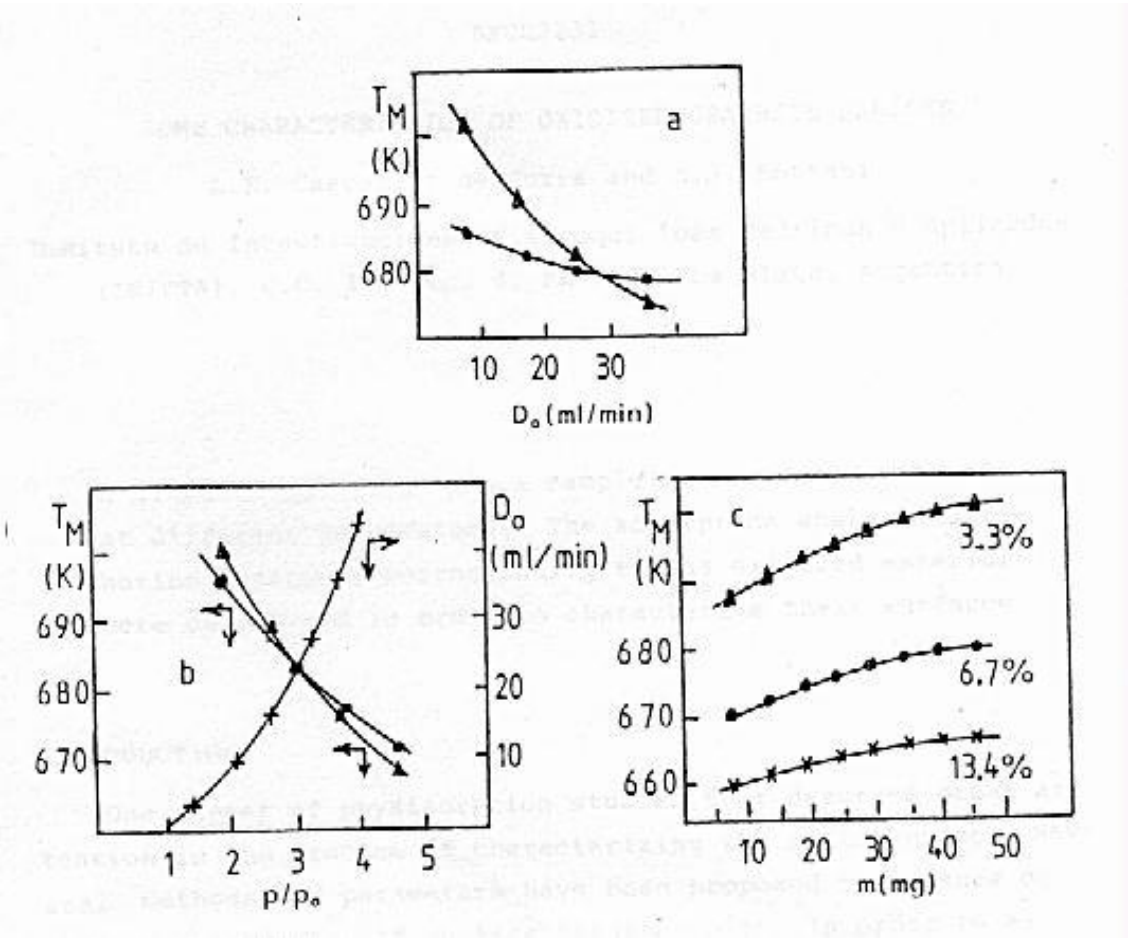


**Figure 2.21: Influence of the various experimental parameters on the TPR peak position**

**a-effect of the flow rate: •-when the pressure is constant, Δ- when the pressure varies like in b(+). b- effect of pressure: • when the flow rate is constant, Δ- when both the flow rate and pressure vary like in curve(+). c- effect of the amount of NiO for different hydrogen concentrations in the reducing mixture.**

# CHAPTER 3

# EXPERIMENTAL METHODOLOGY

## *3.1 CATALYST TESTING REACTOR*

To test the actual performance of the catalysts continuous flow packed bed micro-reactor was used. The advantage of the continuous flow reactor is that the average residence time of the feed stream within the reactor is very short and allows the reactor to handle large volumes of feed stream continuously. The constant reaction conditions may be expected to result in a purer and more reproducible product [64]. In this thesis the type of the reactor was continuously operated packed bed reactor, where feed gases contacted the catalysts.

The reactor was a glass tube reactor with inside diameter 1.5 centimeter. The length of the tube was 48 centimeter. Catalysts were put in between the supports (Calcium carbide). A mixture of 6% $CO_2$, 6% CO, 44% $H_2$, 44% $N_2$ was used as syn-gas. The space velocity of the gas was 10,000 $h^{-1}$. Temperature of the reactor was raised from room temperature until CO fully converted to methane.

### 3.1.1 Gas Chromatograph

Gas chromatography - involves a gas mixture or a sample being vaporized and injected onto the head of the chromatographic column [64]. The sample is transported through the column by the flow of inert, gaseous mobile phase. The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities. The signal from detector shows the composition of feed in the detector.

In this research work Shimadzu GC 17A, TCD was used. The operating conditions of this gas chromatograph was as follows

i) Carrier gas : Argon, 30cc/min

ii) Column temperature: 130°C

iii) Injector temperature: 140°C

iv) Detector temperature: 140°C

v) Column: 3 meter, Activated Charcoal Packed Column.

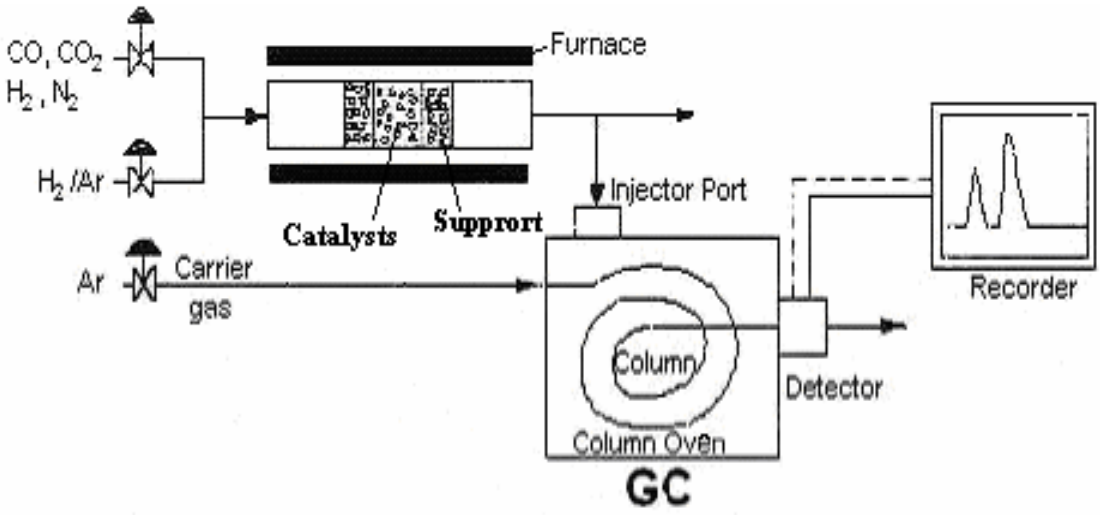


**Figure 3.1: Experimental set up for catalyst testing**

## 3.2 TPR ANALYSIS AND INSTRUMENTATION

For temperature programmed investigation tube electric furnace was used. Temperature was raised up to 1000°C. 10 vol% $H_2$ diluted with Ar was used for reduction of the catalyst. From the computer controlled TPR instrument we can get the reduction profile easily. Below is the general description of the instrumentation of temperature-programmed reduction/oxidation.

Instrumentation for temperature-programmed investigation is relatively simple. Some early TPR studies of catalyst precursors were made using a conventional thermo balance through which a fresh reducing gas was continuously flowed [63, 64]. Others used an arrangement of the type "closed, recirculated atmosphere through a fixed-bed reactor"; the progress of the reaction was monitored by total hydrogen pressure measurement (thermo-manometric method), the water produced by the reduction being condensed into a liquid-nitrogen trap [67]. A schematic representation of a TPR apparatus is presented in Figure 3.2.

The reactor, charged with catalyst, is controlled by a processor that heats the reactor at a rate of typically 0.1-20°C/min. A thermal conductivity detector (katharometer) measures the hydrogen content of the gas mixture before and after reaction. In TPR work, a reducing gas mixture ($H_2$ in Ar or, sometimes, $N_2$) is used. The progress of the reduction is then monitored by the decrease in $H_2$ concentration in the effluent gas.

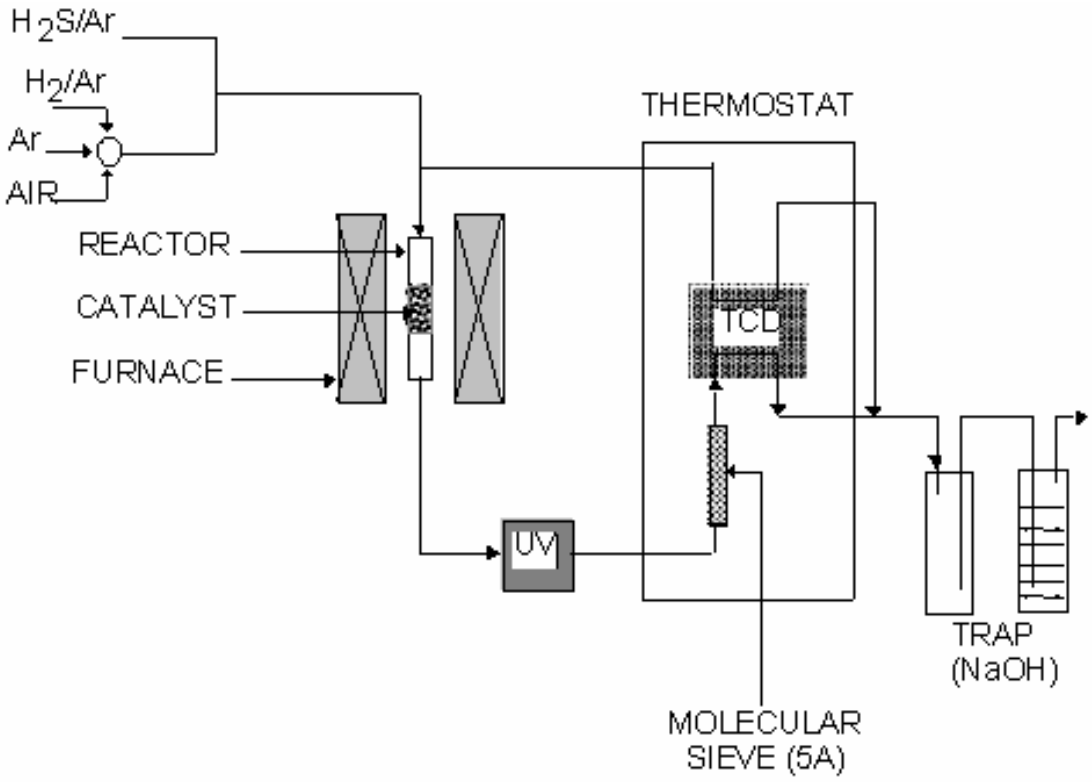


**Figure 3.2: Experimental set up for temperature programmed reduction, sulfidation. [68] The reactor inside the oven, the temperature increased linearly in time.**

## *3.3 CATALYST PREPARATION*

**Materials:**

$Ni(NO_3)_2.6H_2O$; $La(NO_3).6H_2O$; $RuCl_3$; $RhCl_3$; diluted hydrogen(10% $H_2$ in Ar), Reaction gas mixture (6% $CO_2$, 6% CO, 44% $H_2$, 44% $N_2$)

**Preparation:**

γ-Alumina was calcined to 1060°C at a rate of 10°C per minute that converted γ-alumina to θ-alumina. 1060°C is the optimum calcination temperature for high performance methanation catalysts [19]. θ-alumina was used as a support for the catalysts. Ni, $La_2O_3$, Ru, and Rh are the constituents of the catalysts. Weight percent of Ni and $La_2O_3$ were taken 5.0 and 2.7, respectively. These weight percents were shown as optimum amount for methanation catalysts for multi-component catalysts by Inui et al [17]. For Ru the weight percent was varied from 0.2 to 1.0, and Rh was 0.1wt% or 0.2wt%. Incipient wetness impregnation method was adopted for the catalyst preparation. For the metal-salt solution, pure water of 115 vol% of pore volume of θ-Alumina was used. For uniform metal distribution all alumina was dipped into the solution at once. After impregnation, the sample was dried at constant rate of temperature rising from room temperature to 60°C for 2 hours. The sample was then placed in a closed beaker for $NH_3$-$H_2O$ treatment. Amoniacal treatment converts metal salt anion to ammonium salt. Amoniacal treatment increases the activity as shown by Inui et al [69].

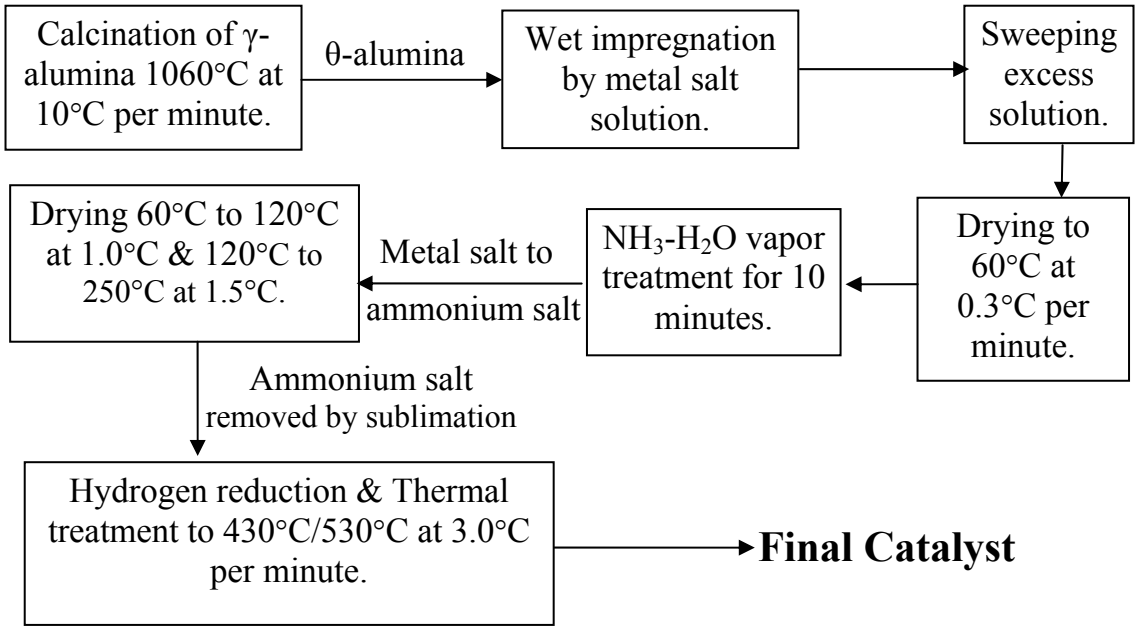


**Figure 3.3 : Block diagram of catalyst preparation**

The $NH_3$-$H_2O$ vapor treated catalysts were then dried from 60 to 120°C for 2 hours, and then temperature was elevated up to 250°C for 1.5 hour. In this step most of the ammonium salts removed by sublimation of nitrate. Hydrogen reduction and thermal treatment was done afterwards. In this step salt-removed catalysts were shifted to a tube electric furnace, and was heated up to 430°C for two hours, in a stream of 10 vol% $H_2$ diluted with $N_2$ with a rate of 6 liter/h. In the case of Ni-$La_2O_3$ the thermal treatment temperature was 530°C. The block diagram of the catalysts preparation is shown in Figure 3.3.

For the multi-component catalysts, precious metals were loaded first. For example, for the preparation of four component catalyst (5wt%Ni- 2.7wt% $La_2O_3$- 0.5wt%Ru- 0.1wt%Rh), the order of impregnation was as follows:

i) Rh was impregnated onto θ-alumina, that was followed by drying, ammoniacal treatment, drying, thermal/reduction treatment.

ii) Ru was impregnated onto Rh impregnated θ-alumina and followed by drying, ammoniacal treatment, drying, thermal/reduction treatment.

iii) Ni-$La_2O_3$ were loaded onto Rh and Ru loaded θ-alumina following same procedure.

# CHAPTER 4

# RESULTS AND DISCUSSION

## *4.1 CHARACTERIZATION BY TEMPERATURE-PROGRAMMED METHOD*

**Ni on θ-alumina**

TPR profile of 5.0 wt% Ni loaded on θ-$Al_2O_3$ and 21wt% Ni on γ-$Al_2O_3$ is shown in Figure 4.1. The reduction temperature of 5.0 wt% Ni on θ-$Al_2O_3$ is 499°C. That is sufficiently high for methanation reactions. On the other hand a TPR profile of a commercial catalyst (20.3wt% Ni on γ-$Al_2O_3$) shows that reduction temperature is 478°C. For commercial catalyst this result is identical to the result of Ahmed et al [68]. This result proves that Ni has a very strong interaction with $Al_2O_3$ that is account for higher reduction temperature. The interaction increases with decreasing loading and increasing reduction temperature. Shalabi et al. [70] showed that after 300°C, methanation decline due to opposing effects of extent of reduction and surface area of Ni crystals. The shoulder peak at 344°C indicates the reduction of some loosely bonded Ni metals with the support.

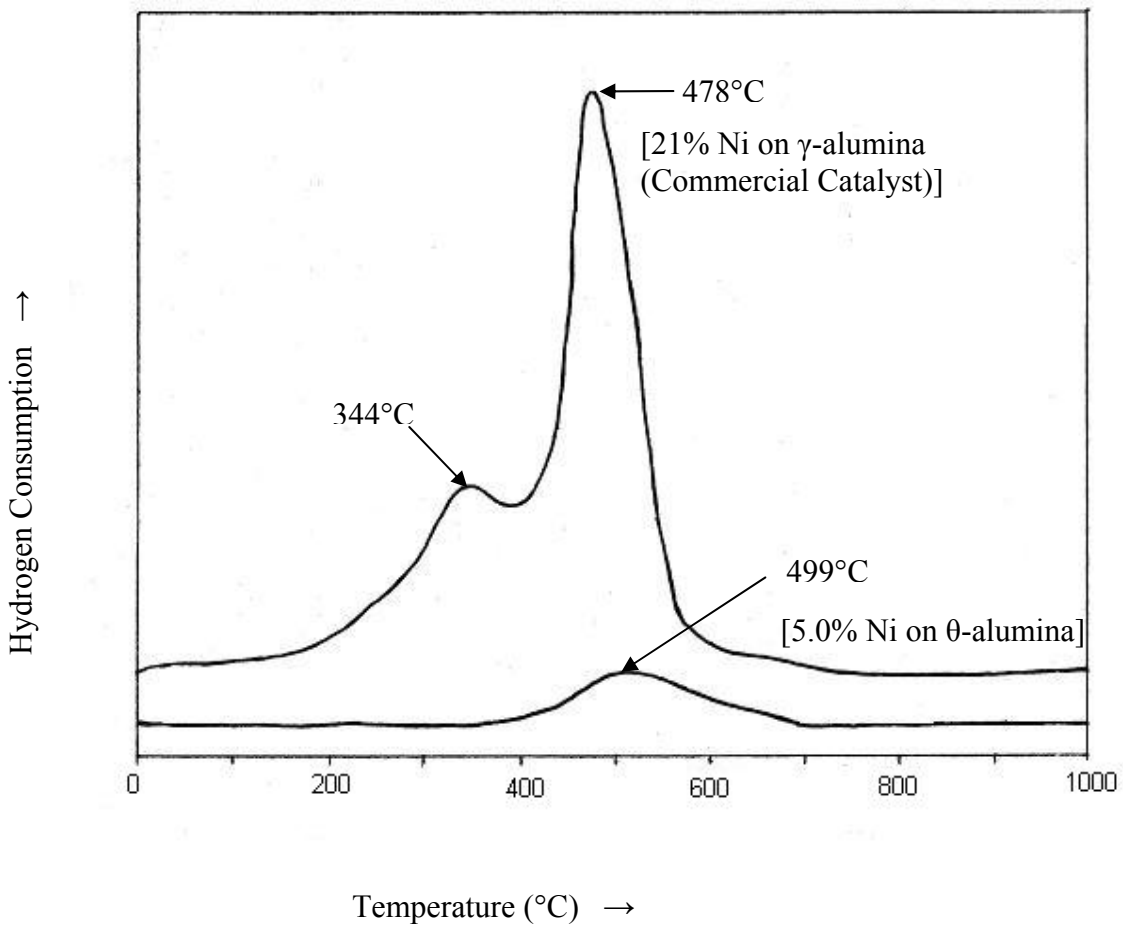


**Figure 4.1 TPR profiles of Ni loaded methanation catalysts.**

Therefore, Ni on $Al_2O_3$ which is conventional methanation catalyst is not suitable for high performance catalyst working at low temperature. The high consumption of hydrogen seen in the TPR profile of the commercial catalyst is due to high amount of hydrogen needed for the reduction of high amount of Ni metal (21%).

**Ni and $La_2O_3$ on θ-alumina**

TPR profile of Figure 4.2 shows adding little amount of $La_2O_3$ (2.7%) with Ni, reduction temperature does not decreased significantly. But methanation reaction increases with addition of $La_2O_3$ that has no activity on methanation separately [18].

**Ru, Rh and $La_2O_3$ on θ-alumina**

The TPR profiles of 0.2wt% Ru, 0.2wt%Rh and 2.7wt%$La_2O_3$ on θ-$Al_2O_3$ are shown in Figure 4.3. Small reduction peaks are seen due to small amount of metals. From this Figure 4.3, it is seen that the lowest reduction temperature is 129°C for Ru. Therefore, it can be said that Ru is more active than Rh.

**Ni and Ru or Rh on alumina:**

TPR profile of 5.0wt% Ni on 0.2wt% Rh loaded alumina shows three reduction peak temperatures along with a broad shoulder. This indicates Ni and various species of Rh and $Rh_2O_3$ reduced at different temperatures.

Again in case of 5.0wt% Ni on 0.2wt% Ru loaded alumina, the TPR profile was found relatively smooth. But the reduction took place in two steps at 286°C and 477°C. It is because Ru and Ni are reduced separately.

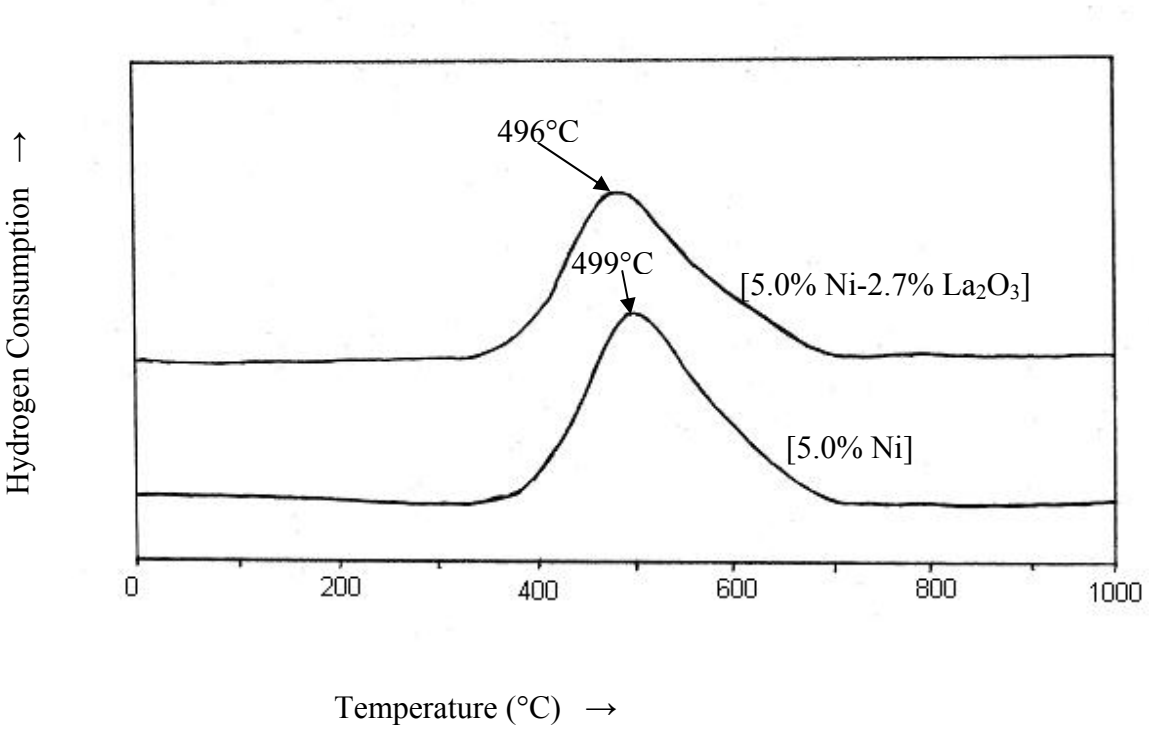


**Figure 4.2 TPR profiles of Ni and Ni-$La_2O_3$ on θ-alumina .**

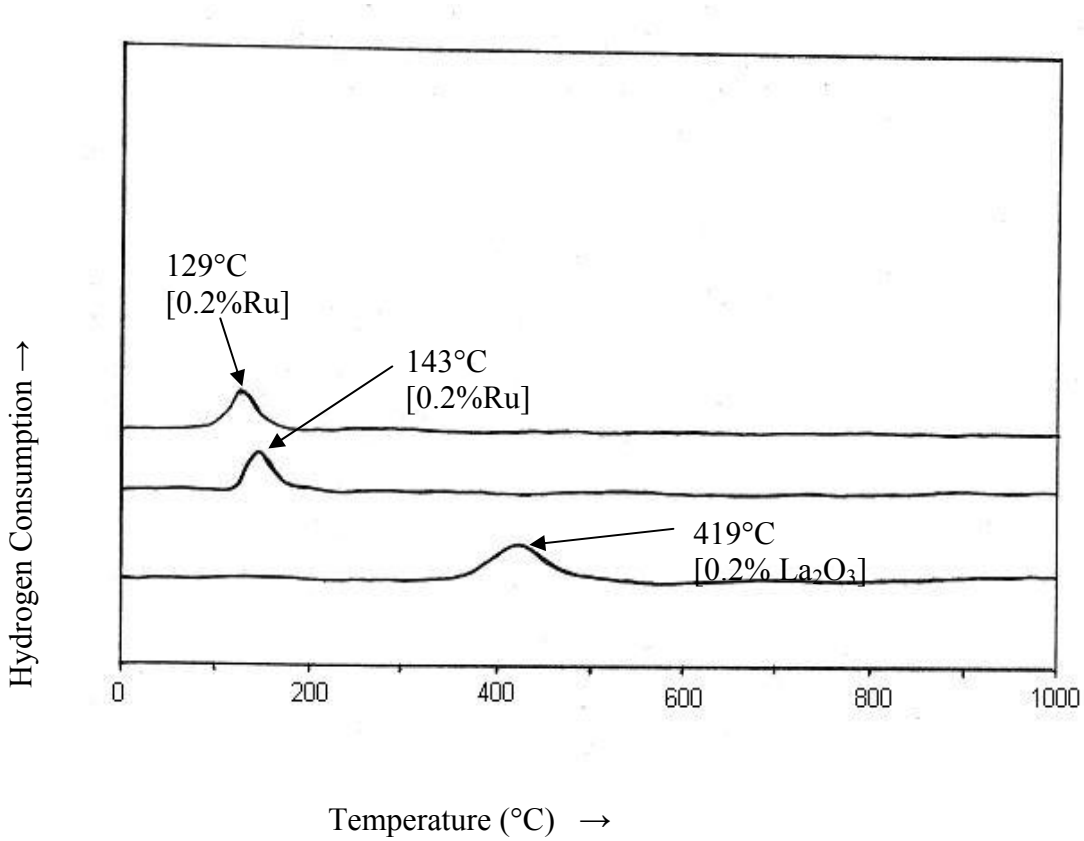


**Figure 4.3 TPR profiles of Ru, Rh and $La_2O_3$ on θ-alumina**

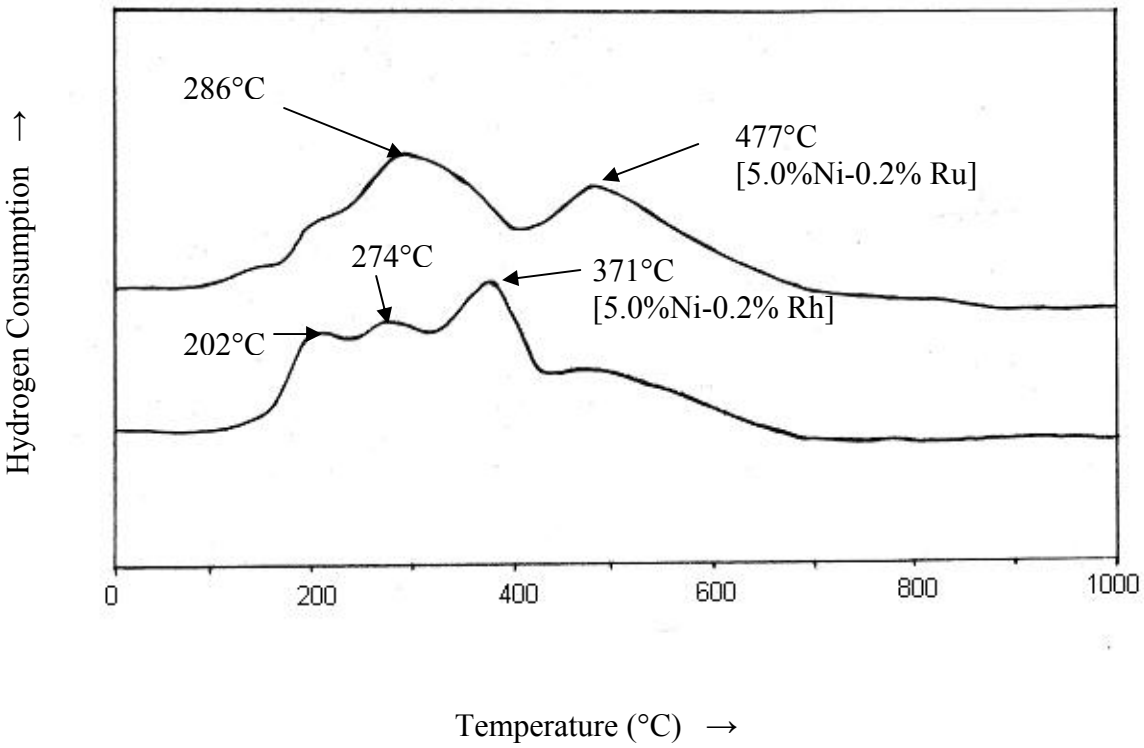


**Figure 4.4 TPR profiles of Ni with Ru or Rh on θ-alumina .**

**Ni-$La_2O_3$-Ru or Rh**

These catalysts were made by adding trace amount (0.2wt%) of platinum group metal (Ru or Rh) with 2.7wt % of $La_2O_3$ and 5wt% Ni loaded on θ-alumina.

In this case the reduction peak temperatures are 382°C for Rh loaded catalyst and 299°C for Ru loaded catalyst [Figure 4.5]. From Figure 4.1 this reduction peak temperature for 5.0wt% Ni was 499°C. The decreased temperatures are due to dispersion of Ni by $La_2O_3$ and the hydrogen spillover effect due to precious metals Ru or Rh.

But the reduction temperature profiles are not smooth. There are significant numbers of shoulders for Rh loaded catalyst. It is due to the growth of two different species of Rh and $Rh_2O_3$ particles; one kind was easily reduced with a high dispersion, and the other kind was harder to reduce with a low dispersion. It is supported by a study conducted by Vis et al[47].

On the other hand, 5.0wt%Ni-2.7wt%$La_2O_3$ on 0.2wt% Ru loaded alumina the profile is smoother and reduction temperature is markedly less (299°C) than that of 5.0wt%Ni-2.7wt%$La_2O_3$ loaded on 0.2wt%Rh. This indicates that Ru is more suitable for methanation catalysts than Rh. Ru disperses more uniformly on support metal.

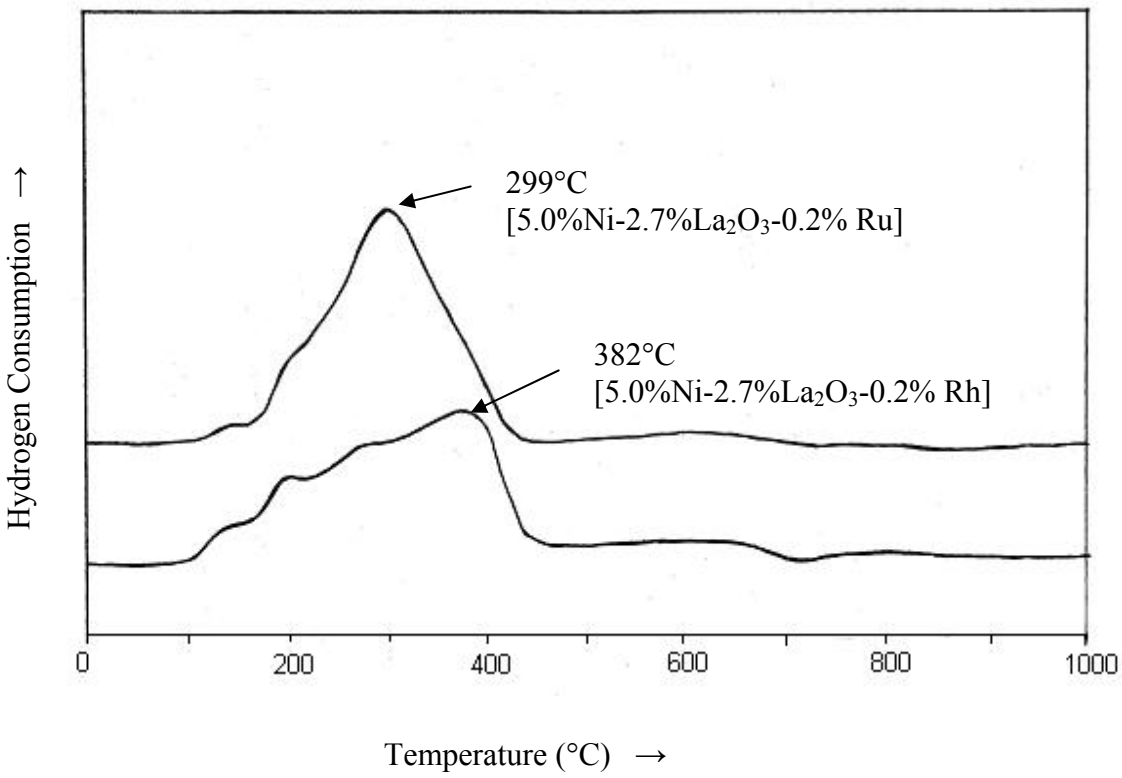


**Figure 4.5 TPR profiles of Ni-La2O3-Ru or Rh on θ-alumina.**

**Ni-$La_2O_3$ on various amount of Ru**

As Ru works very good to reduce reduction temperature, making catalysts by increasing the percentage amount of Ru (0.2 to 1.0 wt %.) was proceeded. It was found that the reduction temperature reduced substantially from 299°C to 233°C [Figure 4.6]. The area increased which suggested high consumption of hydrogen, i.e. better reduction.

But an additional sharp reduction peak appeared at 147°C with increased amount of Ru(1.0wt%) before the complete reduction at 233°C. This indicates a small amount of Ru which was loosely bonded with the catalyst support that reduced prematurely.

Though addition of more Ru reduces reduction temperature, however, excess Ru remained loosely bonded with catalyst. The amount of Ru was then reduced to 0.5wt%. In this case reduction temperature was 284°C. But still a small shoulder was seen with a sharp peak. Consumption of hydrogen also reduced due to less amount of Ru.

Finally, Ru was reduced to 0.2wt%. An acceptable profile was found though consumption of hydrogen further reduced and reduction temperature went to 299°C. This is still a low reduction temperature. The reduction in one step means whole catalyst was reduced simultaneously. This increases catalyst longevity.

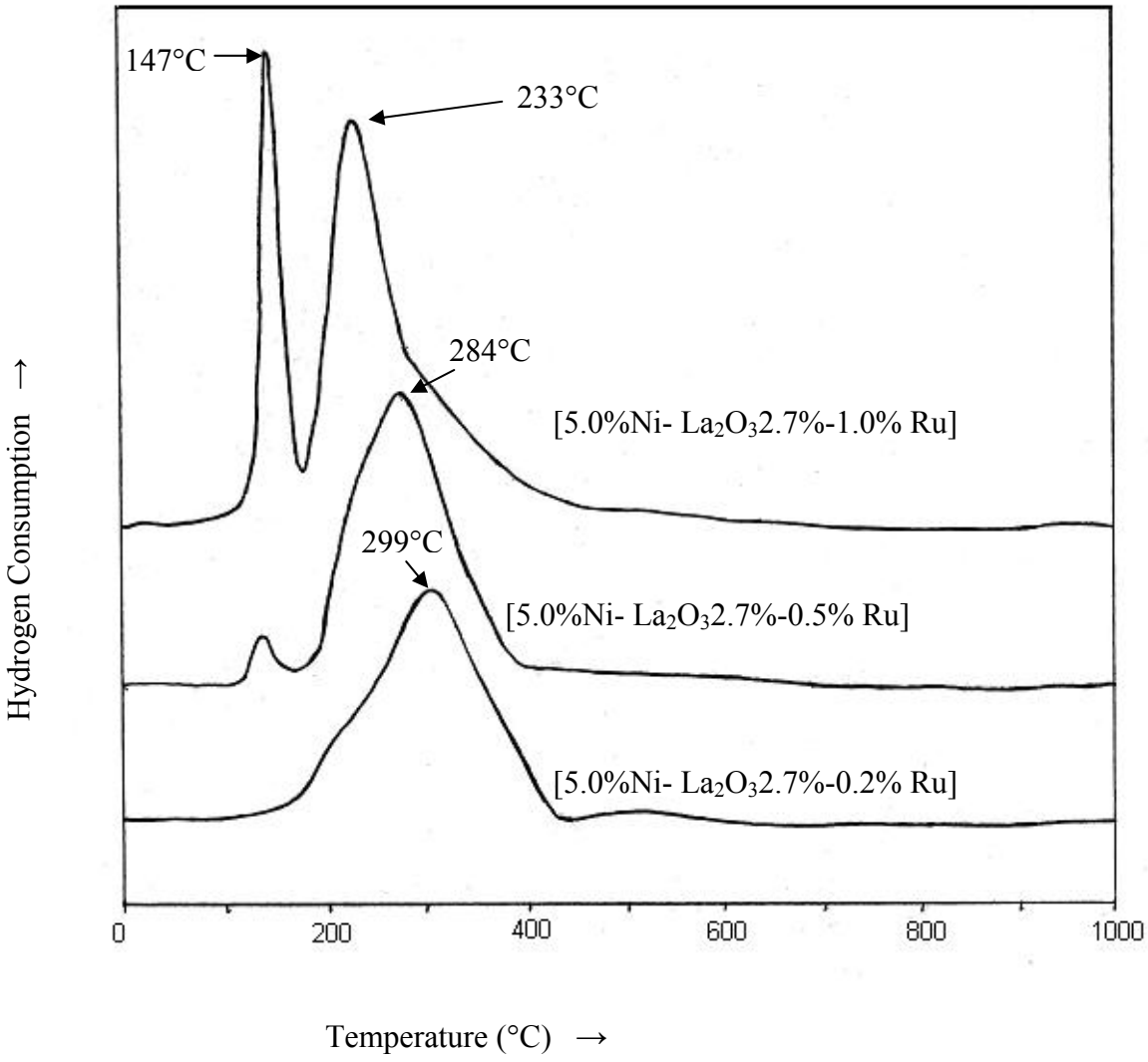


**Figure 4.6 TPR profiles Ni-$La_2O_3$-Ru on θ-alumina.**

**Ni-$La_2O_3$-Ru-Rh**

Three-component catalyst (5.0wt% Ni- 2.7wt% $La_2O_3$- 0.5wt% Ru) was tested in a micro reactor by Inui et al. which was claimed as very high performance catalyst [2]. This catalyst was not characterized by temperature-programmed reduction method. In this thesis work TPR profile [Figure 4.6] of 5.0wt% Ni- 2.7wt% $La_2O_3$- 0.5wt% Ru catalyst showed sharp reduction temperature peak at 284°C with a very small shoulder due to some loosely bonded Ru. However, it can said that uniform distribution of metals and low reduction temperature made this catalyst as a very good catalyst. This verifies the claim of the study by Inui et al. [2].

However, for further development of the high performance catalysts 0.2wt% Rh and 1.0wt% Ru were added respectively before adding 5.0wt%Ni and 2.7wt% $La_2O_3$ on θ-alumina. This was in an assumption that the activity of these methanation catalysts could be increased more by using a little more amount of Ru with a trace amount of Rh. But TPR profile [Figure 4.7] shows two reduction peaks at 142°C and at 250°C. A conclusion was drawn from previous experience [Figure 4.6] that this is for early reduction of Ru metals that are loosely bonded with the catalyst. Therefore, decreasing the amounts of Ru as well as Rh was considered.

Ru was reduced from 1.0wt% to 0.5wt% and Rh from 0.2wt% to 0.1wt%. A large sharp peak was observed with 0.5wt% Ru and 0.1wt%Rh [Figure 4.7]. The reduction temperature was 292°C. It indicates high consumption of hydrogen i.e. high reduction of the metals. It also indicates that all metals in the catalyst fully reduced simultaneously at a very low temperature. The very small peak is due very little amount of loosely bonded Ru metal with the support.

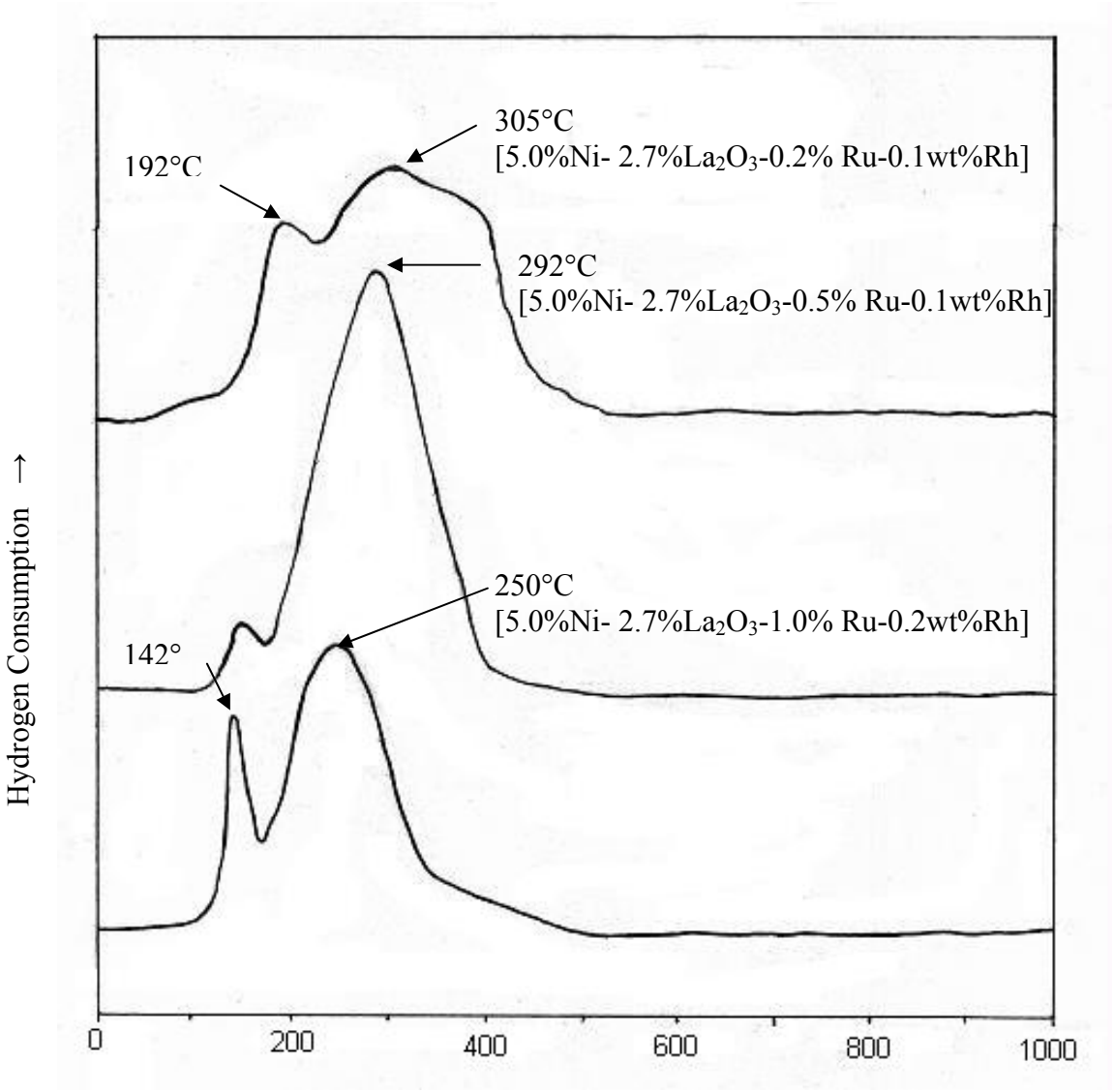


**Figure 4.7 TPR profiles of Ni-$La_2O_3$-Ru-Rh on θ-alumina.**

Precious metals should be used as less as possible. For this reason Ru was further reduced to 0.2wt%. The TPR result [Figure 4.7] showed a broad peak with the highest reduction peak at 305°C. This result is due to the very small amount of Ru and Rh that were dispersed widely on the support.

From the above discussion of TPR profiles it was concluded that if loading of metals were high the dispersion of metals would be deteriorate and reduction took place in different steps. It supports the conclusion made by Thomas et al. [71]. The optimum composition of four component catalysts was concluded as 5.0wt% Ni, 2.7 wt%$La_2O_3$, 0.5wt% Ru and 0.1wt% Rh. This catalyst showed single large sharp peak at lower temperature than commercial catalyst and three component catalysts. Thus it showed best activity.

## 4.2 CATALYST PERFORMANCE EVALUATION

**Testing in a continuous flow micro-reactor**

**Preferential Methanation of CO**

A mixture of 6%$CO_2$, 6%CO, 44%$H_2$, and 44% N2 was passed through a continuous flow micro-reactor packed with catalysts to carry out methanation reaction with a space velocity of 10,000$h^{-1}$. The temperature was of the reactor was raised from room temperature to 500°C.

The temperature dependence preferential methanation of CO is shown in Figure 4.8. The Figure shows methanation of carbon oxides using commercial catalysts and four component catalysts.

From the Figure it is seen that methanation of carbon oxides occurs simultaneously in commercial catalysts while in high performance four component catalyst, methanation of CO occurs first. In commercial catalyst, up to 370°C methanation of CO took place and then methanation of $CO_2$ starts. Therefore preferential methanation by commercial catalysts can occur up to 370°C; but in this case conversion is very low.

On the other hand, in four component catalysts, after complete conversion of CO, methanation of $CO_2$ starts. In this case CO retards the methanation of $CO_2$.

From the Figure 4.8 it is seen that in multi-component methanation catalyst, the methanation reaction temperature is very low compared to commercial catalyst. The selectivity is also high.

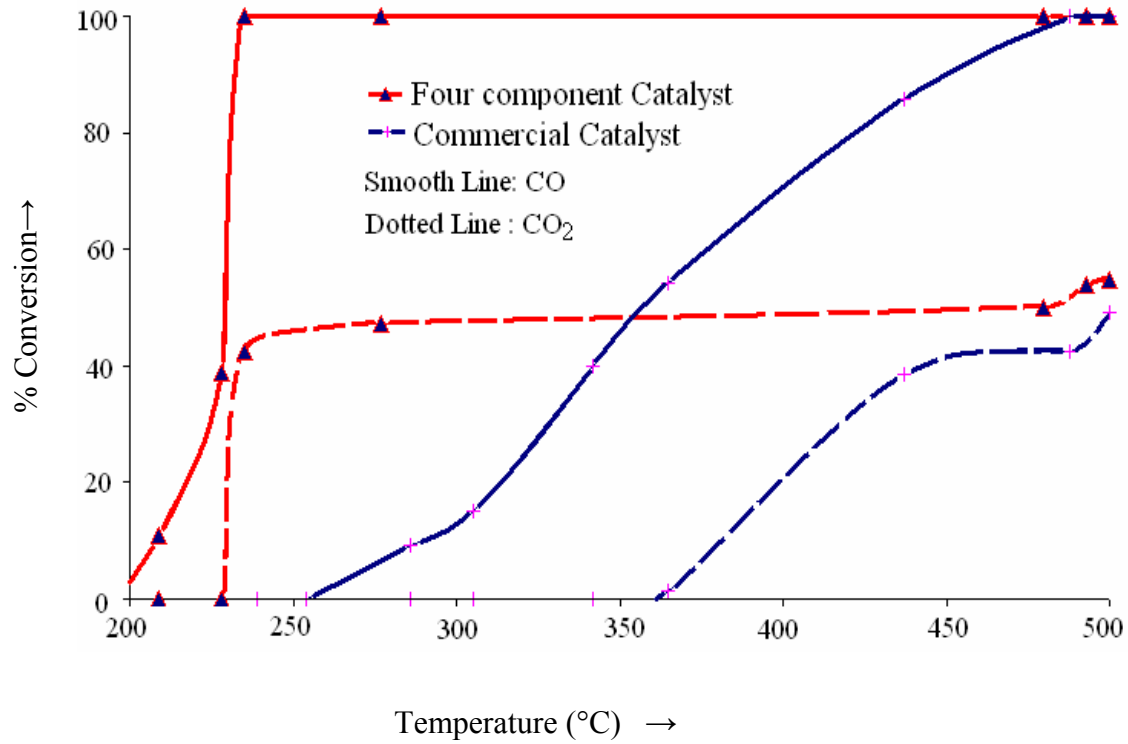


**Figure 4.8 Comparison for the preferential methanation of CO**

**CO-Methanation of carbon oxides:**

The temperature dependence of CO and $CO_2$ conversion using four kinds of catalysts is shown in Figure 4.9.

It is seen that for three and four component catalysts full conversion of CO occurred at very low temperatures that signify very high performance. In coexistence of CO and $CO_2$ the methanation of CO occurred preferentially on every catalyst except the commercial catalyst. For all of the multi-component catalysts the methanation of $CO_2$ proceeded after CO was almost completely consumed. These indicate that the strong adsorption strength of CO during the reaction is far stronger than that of $CO_2$ on multi-component catalysts. The existence of CO inhibits the $CO_2$ methanation. The lowest temperature for full conversion of CO is seen at 230°C on four component catalyst.

On the other hand, commercial catalyst (21wt%Ni on $\gamma$-$Al_2O_3$) shows very high temperature (488°C) for complete methanation of CO. In this case, $CO_2$ starts methanation reaction before the CO completely consumed. That means that this catalyst is not suitable for preferentially removal of CO.

Therefore, multi-component methanation catalysts can be used in processes where preferential removal of CO is necessary.

Among all catalysts four component catalysts are showing the highest performance for preferentially removal of CO.

It is also seen from the Figure 4.9 that $CO_2$ conversion was only around 50% even after 500°C for every catalyst. It is due to the reduced partial pressure of hydrogen by methanation reaction.

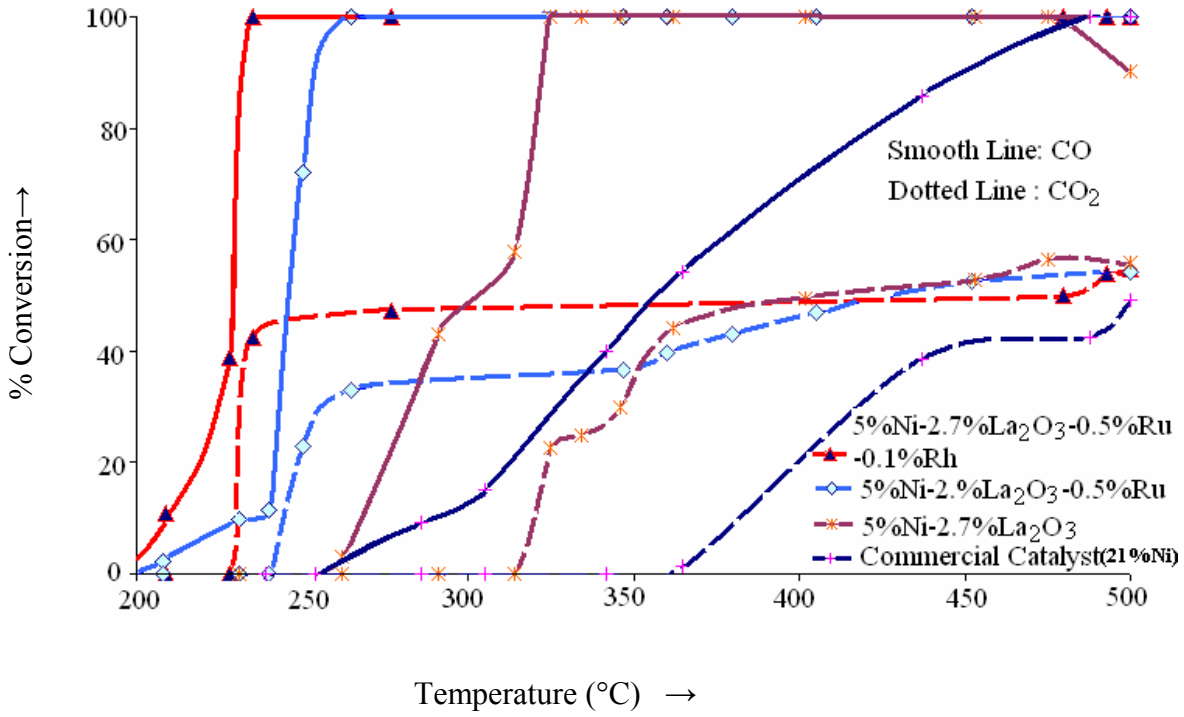


**Figure 4.9 Temperature dependence of CO and $CO_2$ conversion in co-methanation**

**Comparison of four component catalysts**

TPR profiles and Figure 4.9 showed that four component catalysts (Ni-$La_2O_3$-Ru-Rh) are very active in low temperatures. Three kinds of four component catalysts were tested in the reactor. From the literature it was found that so far three component catalyst (5.0wt% Ni-2.7wt%$La_2O_3$-0.6wt%Ru) was the best methanation catalyst [2]. The preferential methanation reaction temperature for full conversion of CO was 250°C [2]. The Figure 4.10 shows that this temperature can be reduced to 230°C for four component catalyst.

Although the temperatures for the full conversion of CO on all four component catalysts are very low [Figure 4.10]; the precious metal should be used as little as possible. Considering this view point Ru and Rh was varied in the preparation of catalysts. From the literature 5.0wt% Ni, 2.7wt% $La_2O_3$ and 0.5wt%Ru was found the best composition for multi-component catalysts [17]. But combination of Ru and Rh was not tested before this research. Even it was not tested what will happen if Ru is reduced below 0.5wt%. The Figure 4.10 shows that 5.0wt%Ni-2.7wt%$La_2O_3$-0.5wt%Ru-0.1wt%Rh can remove CO at the lowest temperature. Increasing Ru from 0.5wt% to 1.0wt% and Rh from 0.1wt% to 0.2wt%, the Figure shows the increased temperature for full conversion of CO, i.e. decreased activity. Moreover, it is the loss of precious metal.

Again, decreasing the amount of Ru from 0.5wt% to 0.2wt% full conversion took place at 250°C. It is identical to the temperature found for three component catalyst (5.0wt% Ni-2.7wt%$La_2O_3$-0.6wt%Ru) for its best performance [17] and Figure 4.9. Therefore it can said that 0.6wt%Ru can be replaced by 0.2wt%Ru and 0.1wt%Rh for the same performance.

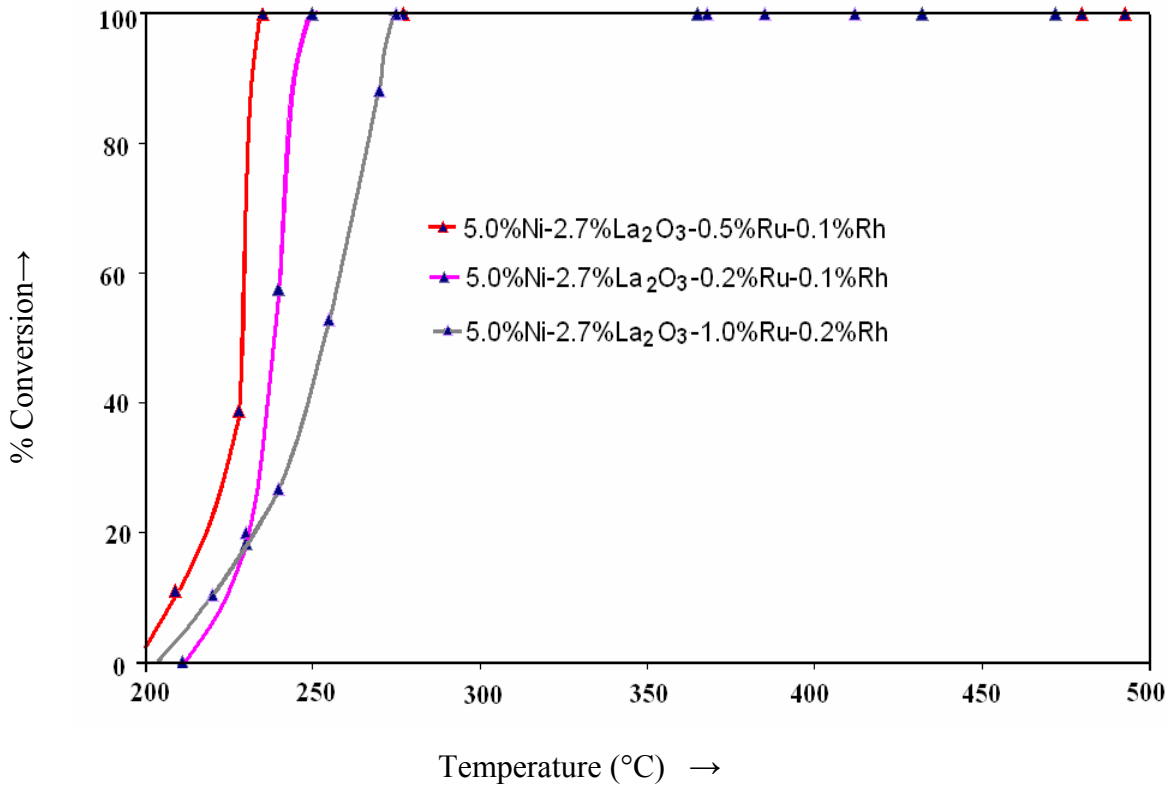


**Figure 4.10 Temperature dependence of CO conversion for 4-component catalysts**

But combination of 0.5wt%Ru and 0.2wt%Rh with 5.0wt%Ni and 2.7wt%$La_2O_3$ the temperature was reduced to 230°C for preferential full conversion of CO.

As discussed before, though Rh with Ru increased the methanation activity for their hydrogen spillover effect, excess of these metals does not increase the activity, rather it is the loss of valuable metals. Again, very small amount can not add activity to the performance. Therefore, there should be a optimum balance in the amount of using precious metals. From the Figure 4.10 it is seen that 0.5wt%Ru and 0.1wt% Rh with 5.0wt%Ni and 2.7wt%$La_2O_3$ are showing best performance.

**Comparison of CO methanation for different catalysts:**

Six kinds of catalysts were tested to see the performance of CO methanation. The Figure 4.11 shows the temperature dependence of CO conversion on different catalysts.

From Figure 4.11 it is seen that methanation of CO started at 250°C for commercial catalysts, but complete conversion was taken place 485°C. In case of 5wt% Ni, the conversion started at 280°C and up to 500°C, 85% conversion took place. But adding 2.7wt% $La_2O_3$ with 5% Ni increased the activity greatly. Before 325°C all CO consumed. Because $La_2O_3$ increased the dispersion of Ni and its basicity, that is the cause for this increased performance [3].

On the other hand, the same Figure shows that adding trace amount (0.5wt %) of platinum group metal Ru with 5wt% Ni increased the activity more. At 290°C all CO consumed. It is for the hydrogen spillover effect of Ru.

For three component catalyst (5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt% Ru) the performance of the catalyst increased markedly. At 260°C all CO consumed. This is for the combined effect of La2O3 and Ru)[Figure 4.11].

The more increased activity was seen for four component catalysts (5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt% Ru-0.1wt% Rh)[Figure 4.11]. In this case at $230^0$C all CO consumed. Conversion at lower temperature indicates higher selectivity and higher energy saving. In this case, increased dispersion and basicity of Ni by $La_2O_3$ associated with hydrogen spillover effects of Ru and Rh. The processes where operation is needed at very low temperature for the preferential removal of CO, this four component catalyst can be used successfully.

The methanation is an exothermic reaction. Temperature increased greatly during the reaction. While using the four component catalysts, after reaching reactor temperature to 230°C, suddenly the temperature rose from 230°C to 480°C within a 20 seconds.

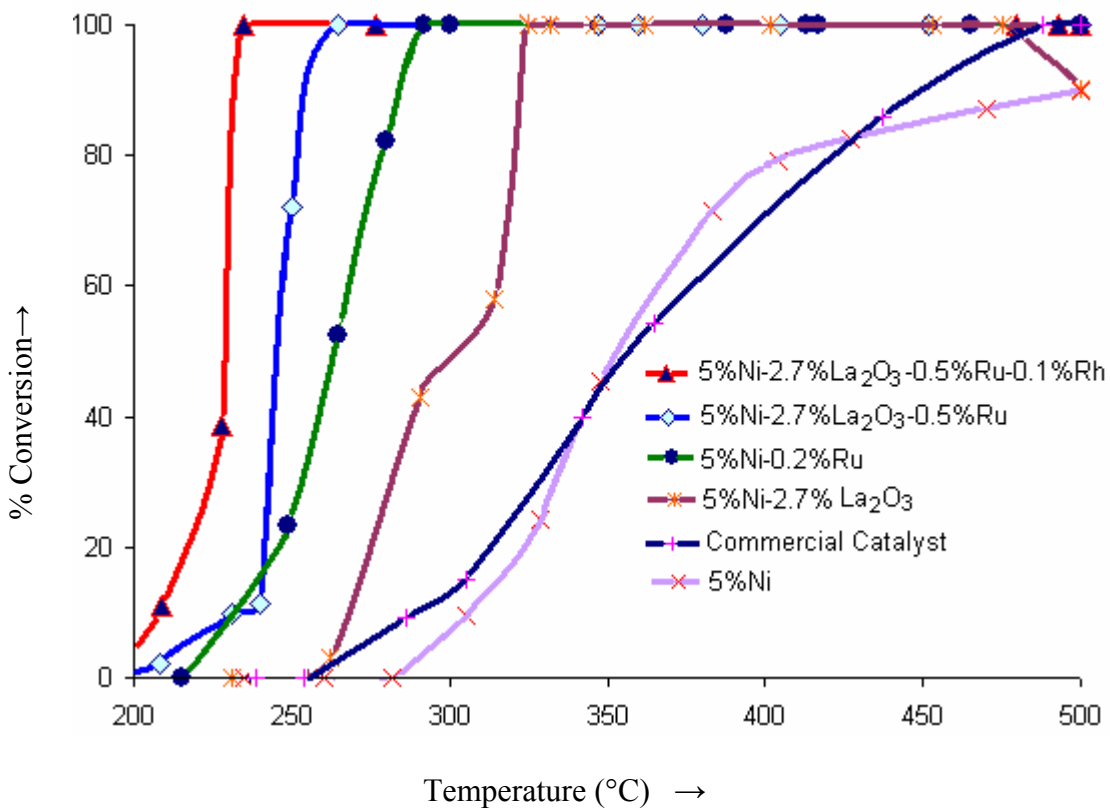


**Figure 4.11 Temperature dependence of CO conversion**

**Comparison of $CO_2$ methanation for different catalysts:**

Methanation of $CO_2$ on various catalysts is shown in Figure 4.12. Conversion of $CO_2$ could not exceed 57%. It is interpreted as the reduction of hydrogen partial pressure by consumption of hydrogen for preferential methanation of CO.

By increasing partial pressure of hydrogen conversion of $CO_2$ can be increased [2]. From the Figure 4.12, it is seen that for four catalysts $CO_2$ consumption was 48% at 235°C and then it reached to plateau level. It is 260°C for three component catalysts. For other catalysts methanation of $CO_2$ increased with temperature but even at very high temperature it could not exceed 57%. On an average, four component catalysts are showing the best performance for $CO_2$ methanation among all other catalysts.

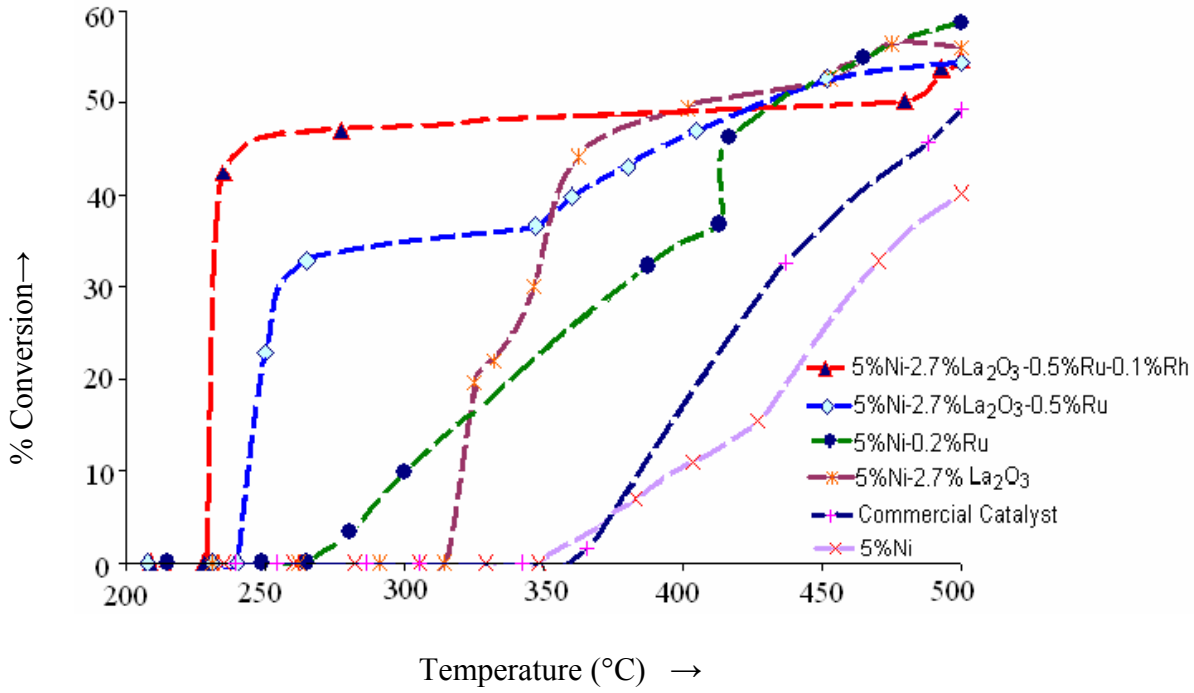


**Figure 4.12 Temperature dependence of $CO_2$ conversion**

# CHAPTER 5

# CONCLUSION

## *5.1 CONCLUSION*

Though methanation of carbon oxides is in use in many catalytic process industries for purification of feed gases, the performance is very low. Therefore lots of research work is going on. So far three component Ni-based composite catalysts were found the best methanation catalyst in the literature. But from this thesis work it is found that four component catalysts with a composition of 5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt%Ru-0.1wt%Rh performed better than three component catalysts.

It has been shown that TPR was used as qualitative method for catalyst inspection, to give information on the influence of support materials, the reduction steps, the amount of reducible species and the temperature peak maxima. Before this research work multi-component composite methanation catalysts were not characterized by TPR study. In this thesis work TPR method helped not only to characterize the catalysts but also to explain the relatively complex concept of hydrogen spillover mechanism.

TPR profiles of some catalysts either showed more than one peak or reduced at high temperatures. Reduction at various temperatures or at high temperatures means low activity.

From the TPR profiles it has been seen that four component catalyst (5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt%Ru-0.1wt%Rh) showed higher activity than any other catalyst prepared for this thesis work. Three component catalysts (5.0wt% Ni-2.7wt% $La_2O_3$-0.2wt%Ru) showed a very good result but could not exceed the overall activity of the four component catalysts. The reduction of four component catalysts was taken place at very low temperature with a sharp peak. This signifies the high activity due to the simultaneous reductions of metal components.

Using the continuous flow micro-reactor for the performance test of the catalysts, it has been found that multi-component catalysts showed very high performance. Full conversion of CO was taken place only at 260°C using three component catalysts (5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt%Ru) and at 230°C using four component catalysts (5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt%Ru-0.1wt%Rh). 230°C is the lowest temperature among all methanation temperature ever found in the literature. In these cases it was also seen that conversion of $CO_2$ starts after full consumption of CO. It is necessary for preferential methanation of CO. Preferential methanation by using commercial catalysts is possible below 370°C, but at this temperature the conversion of CO is very less.

Methanation reaction is exothermic reaction; heat generation during the methanation reaction is very high. This heat can be used as energy source for heating other processes.

Finally it can be concluded that for avoiding poisonous effect of CO, 5.0wt% Ni-2.7wt% $La_2O_3$-0.5wt%Ru-0.1wt%Rh can be used as the potentially best methanation catalyst. It can be used for purification of feed gases from CO.

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# APPENDIX

## *SAMPLE CALCULATION*

**5.0wt%Ni -2.7wt%$La_2O_3$ -0.5wt%Ru -0.1wt%Rh in 5.0gm θ-alumina**

Impregnation order is as follows:

i) Rh ii) Ru iii) Ni+$La_2O_3$

Molecular weight of $RhCl_3$(98%) = 209.26

Molecular weight of Rh = 102.9055

Formula weight of $RuCl_3$ = 207.43

Molecular weight of Ru =101.07

Molecular weight of $Ni(NO_3)_2.6H_2O$ = 290.81

Molecular weight of Ni = 58.70

Molecular weight of $La(NO_3).6H_2O$ = 433.0117

Molecular weight of $La_2O_3$ = 325.8092

According to weight percent (5.0wt%Ni -2.7wt%$La_2O_3$ -0.5wt%Ru -0.1wt%Rh) loaded on alumina in 100 gm catalyst the weight of different metals are

Rh = 0.1 gm

Ru = 0.5 gm

$La_2O_3$ = 2.7 gm

Ni = 5.0 gm

θ-alumina = 91.7 gm

For 91.7 gm alumina Rh needed 0.1 gm

For 5.0 gm alumina Rh needed $\frac{0.1x5.0}{91.7}$ gm

$= 0.00545$ gm

102.9055 gm Rh can be got from 209.26 gm $RhCl_3$

0.00545 gm Rh can be got from $\frac{209.26x0.00545}{102.9055}$ gm $RhCl_3$

$= 0.01109$ gm $RhCl_3$

Purity of $RhCl_3$ is 98%

Therefore, $RhCl_3$ needed $\frac{0.01109}{0.98}$ gm $RhCl_3$

$= 0.0113$ gm $RhCl_3$

For 91.7 gm alumina Ru needed 0.5 gm

For 5.0 gm alumina Ru needed $\frac{0.5x5.0}{91.7}$ gm

$= 0.0273$ gm

101.07 gm Ru can be got from 207.43 gm $RuCl_3$

0.0273 gm Ru can be got from $\frac{207.43x0.0273}{101.07}$ gm $RuCl_3$

$= 0.056$ gm $RuCl_3$

For 91.7 gm alumina $La_2O_3$ needed 2.7 gm

For 5.0 gm alumina $La_2O_3$ needed $\frac{2.7x5.0}{91.7}$ gm

$= 0.1472$ gm

325.8092 gm $La_2O_3$ can be got from 433.0117 gm $La(NO_3)_3.6H_2O$

0.1472 gm $La_2O_3$ can be got from $\frac{433.0117x0.1472}{325.8092}$ gm $La(NO_3)_3.6H_2O$

$= 0.1952$ gm $La(NO_3)_3.6H_2O$

For 91.7 gm alumina Ni needed 5.0 gm

For 5.0 gm alumina Ni needed $\frac{5.0x5.0}{91.7}$ gm

$= 0.2726$ gm

58.70 gm Ni can be got from 290.81 gm $Ni(NO_3)_2.6H_2O$

0.1472 gm Ni can be got from $\frac{290.81x0.2726}{58.70}$ gm $Ni(NO_3)_2.6H_2O$

$= 0.1952$ gm $Ni(NO_3)_2.6H_2O$

# Vatae
# of
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| | |
|---|---|
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## PUBLICATION/CONFERENCE

1. Muhammad B. I. Choudhury, Shakeel Ahmed, Mazen shalabi, Tomouki Inui, "*Characterization of multi-component methanation catalysts by Temperature Programmed Reduction method to develop novel type methanation catalyst*", Catalysts in Petroleum Refining & Petrochemicals,14th Annual Saudi-Japanese Symposium, KFUPM Research Institute, Dhahran-31261, Saudi Arabia, December, 2004.
2. Unpublished Masters dissertation on "Studies on High Performance Ni-Based Composite Catalysts for Preferential Methanation of CO in a Syngas" (A paper is in progress for the journal "**Applied Catalysis: A**").